# PHILIPPINE
JOURNAL
OF
SCIENCE

CHEMICAL AND
GEOLOGICAL SCIENCES

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1913
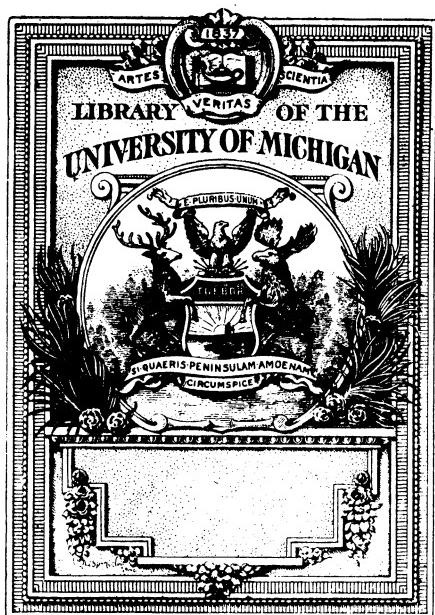
THE PHILIPPINE
JOURNAL OF SCIENCE

ALVIN J. COX, M. A., PH. D.

GENERAL EDITOR

SECTION A

CHEMICAL AND GEOLOGICAL SCIENCES
AND THE INDUSTRIES

EDITED WITH THE COÖPERATION OF

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VOLUME VIII

1913

WITH 54 PLATES, 38 TEXT FIGURES, AND 4 MAPS
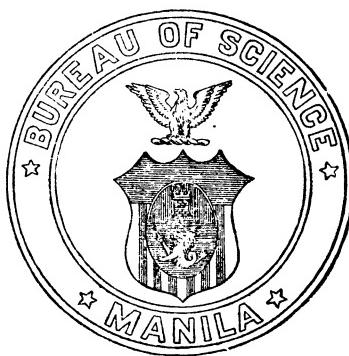
MANILA
BUREAU OF PRINTING
1913

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METHYL SALICYLATE IV.[1] THE SAPONIFICATION OF METHYL SALICYLATE, METHYL BENZOATE, AND THE METHYL ETHER OF METHYL SALICYLATE

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Five text figures

In the first paper on this subject it was shown that salicylic acid could be accurately determined in the presence of its methyl ester by first adding an excess of sodium hydrogen carbonate solution, which will unite with the acid to form sodium salicylate, and then shaking out the ester with a suitable solvent such as chloroform. The principle of this separation depends upon the fact that the rate of saponification of the ester by sodium hy-

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[1] I. The separation of salicylic acid from methyl salicylate and the hydrolysis of the ester, by H. D. Gibbs, *This Journal, Sec. A* (1908), **3**, 101; *Journ. Am. Chem. Soc.* (1908), **30**, 1465; II. Solubility in water at 30°, by H. D. Gibbs, *This Journal, Sec. A* (1908), **3**, 357; III. The coloration of methyl salicylate and some allied compounds in the sunlight, by H. D. Gibbs, R. R. Williams, and D. S. Pratt, *ibid* (1912), **7**, 79.

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drogen carbonate is negligible since the concentration of sodium hydroxide in the solution is very small.[4]

Preliminary comparisons of the rate of saponification of the ester with sodium hydroxide, sodium carbonate, and sodium hydrogen carbonate showed that the first was fairly rapid, the second was very slow, and the last had an almost infinitesimal speed.

Calculations, by means of the formula,[5]

$$N = \frac{\log \left(\frac{dC}{dt}\right)_v - \log \left(\frac{dC}{dt}\right)_V}{\log C_v - \log C_V},$$

from two different sets of data, gave the values 0.994 and 1.028, average 1.011, which signified that the reaction between an excess of methyl salicylate and sodium hydroxide was of the first order. The velocity constants obtained were very unsatisfactory and since, at that time, they were not necessary for the purposes in hand, they were not mentioned and no explanation was attempted. In this paper much of the preliminary work has been repeated with greater accuracy, the investigation extended to include methyl benzoate and the methyl ether of methyl salicylate, and explanations of the peculiar phenomena involved are offered.

Methyl salicylate is capable of a variety of reactions, several of which occur simultaneously in alkaline solution, and affect the velocity of saponification more or less markedly. Of these, the following have been noted and studied, and are doubtless the most important if not the only reactions occurring in alkaline solution: (1) The splitting of the carboxyl group with formation of carbon dioxide, methyl alcohol, and phenol; (2) the formation of a colored compound in presence of sunlight and oxygen;[6] (3) the substitution of a metal atom for the hydrogen of the phenol group with formation of a salt of the methyl ester, which in water solution is capable of a considerable hydrolysis.

The splitting with formation of carbon dioxide is a reaction which salicylic acid undergoes very readily at higher temperatures,[7] but which had not been noted in the case of the methyl

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[4] The significance of the concentration of sodium salt of methyl salicylate in the solution will be pointed out later in this paper. This factor is negligible in the analytical separation.

[5] Van't Hoff, Vorlesungen über theoretische und physikalische Chemie. Braunschweig (1901), 1, 194.

[6] Methyl Salicylate III, *loc. cit.*

[7] Meyer u. Jacobson, *Org. Chem.* (1894), 2, 629.

ester.   The formation of the colored compound has a very slight effect on the rate of saponification even in the light.

The third reaction, that of the formation of a salt of the ester, has been studied [8] and is responsible for some of the most interesting derivatives of this substance.   It has been of special interest historically because of the analogy of these salts to those of acetoacetic ether.   The same reactivity of the phenol group is exhibited by the free acid [9] and its salts as well as by the ester.   Therefore, the rate of saponification of the ester is also affected by the formation of basic salicylates C_6H_4 (OM) COOM.

Lastly must be taken into account the limited solubility of methyl salicylate which renders the system nonhomogeneous during saponification unless carried out with low concentrations. Saponification in nonhomogeneous systems has been studied by Kremann [10] in the case of ethyl benzoate.

The saponification of methyl salicylate with sodium hydroxide has been carefully investigated by Goldschmidt and Scholz in one of their series of papers.[11]   However, it was seen that the problem could be attacked from a different standpoint and some corrections made in their formula as applied to methyl salicylate.   The work of Goldschmidt and Scholz will be taken up again in the discussion of our own results.

I. CARBON DIOXIDE FORMATION

An experiment was first carried out to determine if carbon dioxide was formed from methyl salicylate at low temperature, and, if so, under what conditions and to what extent.

[8] Graebe, *Ann. Phar.* (1866), **139**, 134; Schreiner, *Ann. d. Chem.* (1879), **197**, 19; Freer, *Am. Chem. Journ.* (1892), **14**, 411; Nicola, *Chem. Centralbl.* (1907), **2**, 49.

[9] Piria, *Ann. d. Chem.* (1855), **93**, 262; Lajoux et Grandval, *Compt. rend. Acad. sci.* (1893), **117**, 44; Adam, *Bull. Soc. chim.* (1894), **11**, 204; Kellas, *Zeitschr. f. physik. Chem.* (1897), **24**, 220; Imbert et Astruc, *Compt. rend. Acad. sci.* (1900), **130**, 35; Buroni, *Gazz. chim. ital.* (1902), **32**, 311; Ley und Erler, *Zeitschr. f. elek. Chem.* (1907), **13**, 797; de Coninck, *Compt. rend. Acad. sci.* (1907), **144**, 757, 1118; Goldschmidt und Scholz, *Ber. d. deutschen chem. Ges.* (1907) **40**, 624; Kailan, *Monatsh. f. Chem.* (1907), **28**, 115; Thül und Roemer, *Zeitschr. f. physik. Chem.* (1908), **63**, 711.

[10] *Monatsh. f. Chem.* (1905), **26**, 315.   See also Reicher, *Ann. d. Chem.* (1885), **228**, 285.

[11] *Ber. d. deutschen chem. Ges.* (1907), **40**, 636.   See also Kellas, *Zeitschr. f. phys. Chem.* (1909), **66**, 81; (1909), **67**, 257; and Finlay and Turner, *Journ. Chem. Soc.* (1905), **87**, 747.

Pure sodium hydroxide was prepared by the following method. Pure metallic sodium freed from oxide, carbonate, and hydrocarbons so far as possible was introduced into a test tube, the bottom of which was connected to a mercury pump by a piece of narrow glass tubing about 3 millimeters internal diameter and from 0.5 to 1 meter long. A slight constriction was made in this tube near the test tube. The end of the test tube was then sealed, and the whole exhausted and warmed to drive off hydrocarbon vapors. After sealing the narrow tube near the pump, the sodium was melted and allowed to flow by gravitation through the constriction, thus filling the tube with pure metallic sodium, the crust of oxide and carbonate being held back. Pieces of this tube were broken off and quickly dropped through the hole of a rubber stopper into a flask of pure water, the atmosphere over which had been replaced by hydrogen. A rapid current of hydrogen was passing through the flask when it was opened to admit the sodium. After the sodium had dissolved, the flask was opened and quickly substituted for flask *D* (fig. 1), the apparatus in the meantime having been freed from any carbon dioxide by a soda-lime tube connected at *A* and sticks of caustic soda in the flask *D*. It was found on acidifying, boiling, and carrying the gases with a stream of hydrogen into barium hydroxide solution, forced from a bottle into *F*, through stopcock *G*, and thus obtained pure, that no trace of carbon dioxide was evolved from the sodium hydroxide thus prepared. *C* and *E* are condensers for holding back vapors of the boiling liquid. Two experiments were made with such a solution. In the first, about 0.5 gram of sodium as hydroxide was allowed to react for fifteen hours at room temperature with a small excess of the ester introduced through the funnel *B*. At the end of this time the solution was acidified with sulphuric acid, boiled, and the vapors passed into the barium hydroxide solution. A slight precipitate of barium carbonate was formed. A second experiment, carried out in the same manner except that the alkali was allowed to react with the ester overnight at 50°, produced a much larger precipitate of barium carbonate. By comparing the volume of this precipitate with precipitates from measured quantities of N/50 $NaHCO_3$ solution in tubes of approximately the same diameter, it was estimated to represent 0.3 to 0.5 milligram of carbon dioxide.

An experiment with 5 grams of the ester and 100 cubic centimeters of N/10 sulphuric acid showed that the carboxyl group
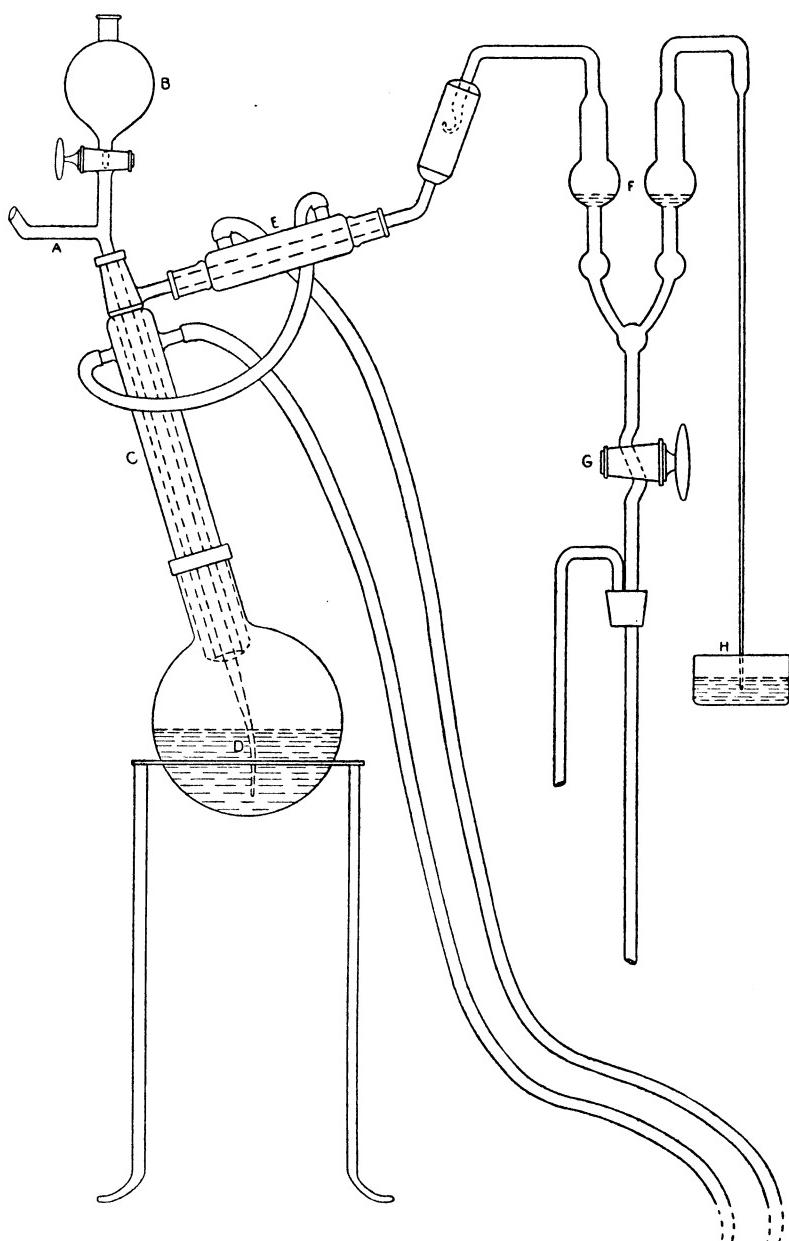
Scale 1 = 4 Cm

FIG. 1.—Apparatus for detecting carbon dioxide formation.

is not split by boiling in dilute acid solution. This proves that the carbon dioxide is a result of the alkaline hydrolysis and probably from salts, rather than from the ester itself.

A further proof of this statement is found in the following experiment. A sealed tube containing salicylic acid and N/10 sulphuric acid was heated on a steam bath in the dark for eight months without the formation of any color and with no appreciable internal pressure. The absence of color is an indication that no carbon dioxide is split off. If phenol were formed, it is probable that some color would be produced by the oxidation of phenol to quinone.[12] The extent to which the splitting of carbon dioxide takes place in alkaline solution is so small as to render carbon dioxide formation a negligible factor of the rate of saponification at ordinary temperatures.

II. THE FORMATION OF SODIUM METHYL SALICYLATE AND ITS HYDROLYSIS

The influence of sodium methyl salicylate on the rate of saponification depends upon the degree of hydrolytic dissociation of the salt in water solution. Goldschmidt has calculated the value for r in the following equilibrium equation to be 0.001.

$$\frac{C_{NaOH} \times C_{C_6H_4 \cdot OH \cdot COOCH_3}}{C_{C_6H_4 \cdot ONa \cdot COOCH_3}} = r.$$

His method was to determine the affinity constant of the phenol group of the ester and to obtain the hydrolytic constant of the salt from the relationship

$$\frac{K_W}{K_B \times K_E} = r$$

in which K_W, K_B, and K_E are the affinity constants of water, the base (diethylamine), and the ester, respectively. It was thought advisable to determine the hydrolytic constant of sodium methyl salicylate by a more direct method. If methyl salicylate be dissolved in pure aqueous sodium hydroxide, after the first moment of time, the following substances are present, the con-

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[12] The compounds which cause the red color in phenol, by Gibbs, *This Journal, Sec. A* (1908), **3**, 361, and The oxidation of phenol, *ibid.* (1909), **4**, 133.

centrations of which may be represented by the symbols opposite them.

Free base (NaOH)	n
Free ester ($C_6H_4 \cdot OH \cdot COOCH_3$)	e
Sodium methyl salicylate ($C_6H_4 \cdot ONa \cdot COOCH_3$)	m
Mono-sodium salicylate ($C_6H_4 \cdot OH \cdot COONa$)	s
Di-sodium salicylate ($C_6H_4 \cdot ONa \cdot COONa$)	d

Let a = the total concentration of sodium atoms and i = the total concentration of radicals containing the benzene grouping. Let x = the concentration of sodium titrated as combined when Congo red is employed as indicator. Then the following relations are true.

$$\frac{en}{m} = r \tag{1}$$

$$\frac{ns}{d} = r' = 0.03 \text{ (Goldschmidt)} \tag{2}$$

$$x = s + d \tag{3}$$

$$a - x = m + n + d \tag{4}$$

$$i = m + e + s + d. \tag{5}$$

Equation (1) represents the hydrolytic equilibrium of sodium methyl salicylate. Equation (2) represents the equilibrium for di-sodium salicylate, and Goldschmidt's average experimental value of 0.03 is used as the hydrolytic constant. Equations (3), (4), and (5) follow from the fact that, with most indicators such as Congo red, the sodium in the phenol position is titrated as free.

Solving the above five simultaneous equations,

$$r = \frac{0.03 \ e \ (a - i + e)}{(e + 0.03) \ (i - x - e)}. \tag{6}$$

a can be determined by previous titration of the sodium hydroxide solution, i by the colorimetric method for salicylic acid after complete saponification, and x by titration at any time when the system has attained equilibrium, disregarding the progress of the saponification. For determining e, two methods are applicable: The first, by using an excess of the ester in which case e will be equal to the maximum solubility, about 0.005 molar; and the second, according to Farmer and Warth,[13] by means of its partition between water and an immiscible solvent. '

[13] *Trans. Chem. Soc. London* (1901), **79**, 863; *ibid.* (1904), **85**, 1713.

For our experiments, a sample of ligroine free from benzene hydrocarbons was used. For determining the partition coefficient, 500 cubic centimeters of pure water were shaken at 30° with 25 cubic centimeters of ligroine in which a weighed amount of ester was dissolved. After two hours' shaking, the water was siphoned off and colorimetric determinations were made of the methyl salicylate in 10 cubic centimeters of each layer.

Experiment No.	Ester per cc. of ligroine.	Ester per cc. of water.	Partition coefficient.
1	0.08962	0.00064	140.0
2	0.06300	0.00048	131.2
3	0.07977	0.00060	132.8
Average			134.7

Therefore, the concentration of methyl salicylate in the ligroine will be about 135 times that in the water under the conditions stated.

In order to determine the hydrolytic constant of sodium methyl salicylate, experiments were carried out under the same condition as above, except that pure dilute aqueous sodium hydroxide of known titre was substituted for the water. a, i, and x were determined by the methods given above; e was taken as 1/135 times the concentration of methyl salicylate in the superincumbent ligroine layer. The data obtained follow. r was calculated from equation (6).

	No. 1.	No. 2.
$a =$	0.0159	0.0638
$x =$	0.0072	0.0155
$i =$	0.0114	0.0600
$e =$	0.0005	0.0059
$r =$	0.00066	0.00124

Experiments by the method of maximum solubility were carried out as follows. About 5 grams (a large excess) of methyl salicylate were shaken for about two hours at 30° with about 25 cubic centimeters of standard sodium hydroxide with the following results:

	No. 1.	No. 2.
$a =$	0.0993	0.0993
$x =$	0.0483	0.0481
$i =$	0.0970	0.0971
$e =$	0.005	0.005
$r =$	0.00072	0.00070

a, x, and *i* were determined as before, and *e* taken as 0.005, the maximum solubility.

While neither method is capable of great accuracy, still the four values of *r* computed according to equation (6) confirm Goldschmidt's result of 0.001 as substantially correct.

III. THE EFFECT OF NONHOMOGENEITY ON THE RATE OF SAPONIFICATION

THE SAPONIFICATION OF METHYL BENZOATE

For this purpose the reaction of methyl benzoate with sodium hydroxide was first studied. This reaction is a bimolecular one when it takes place in a homogeneous medium. When, however, the hydrolysis takes place in aqueous solution in which the ester is but slightly soluble, the reaction proceeds sensibly as a monomolecular one. This has already been pointed out by Kremann [14] in the case of ethyl benzoate and amyl acetate which he took as typical representatives of the class of difficultly soluble esters. He failed to point out the mathematical basis for the observations, contenting himself with a statement of the uselessness of such observations as a means of learning the mechanism of the reaction.

The mathematical basis is very evident. A bimolecular reaction is one in which the velocity is proportional to the concentrations of two variables. When one of the reacting substances is sparingly soluble its concentration is limited by its solubility; that is, the amount transposed is immediately replaced if an excess is always present, unless the velocity of solution be less than that of transformation. Then the equation for a bimolecular reaction becomes $\frac{dx}{dt} = K(a - x)(b - x + x)$, in which *a* and *b* are the original concentrations, *x* is the quantity of each transposed at the time *t*, and $(b-x+x)$ is a constant limited by the solubility of the ester. That is, one variable may be regarded as disappearing, and the equation becomes $\frac{dx}{dt} = K_1$ $(a - x)$ in which $K_1 = K$ times the molecular solubility of the free ester. Kremann's results would have shown this more clearly if he had used an excess of the ester so that the concentration would remain the same to the end of the reaction. If this is done, the value for K_1 remains constant, as is shown in the case of the methyl ester in the following experiment.

[14] *Monatsh. f. Chem.* (1905), **26**, 315.

TABLE I.—*Saponification of methyl benzoate with NaOH 0.0920 Normal. T=30°±0.1°   Corallin indicator.*

t minutes.	a − x.	K_1.	$K = \dfrac{K_1}{0.01568.}$
0	0.0920	----------	----------------
6	0.0610	0.0685	4.369
12	0.0400	0.0693	4.420
17	0.0280	0.0699	4.458
23	0.0180	0.0709	4.522
28	0.0125	0.0711	4.535
33	0.0085	0.0720	4.592
38	0.0058	0.0725	4.624
43	0.0042	0.0718	4.579
50	0.0027	0.0705	4.497
63	0.0015	0.0654	4.172
78	0.0005	0.0668	4.261
Average computed after discarding the first one and last two values		0.0710	4.529

In order to compute K from K_1, determinations of the solubility of methyl benzoate in water were made.

Freshly boiled, distilled water and pure methyl benzoate were employed for the purpose. The water and an excess of the ester were shaken violently, producing an emulsion, for three hours at 30° in glass-stoppered bottles. Twenty-five cubic-centimeter portions of the water were then saponified in the cold with standard sodium hydroxide solution, and the excess titrated. The following values were obtained.

Experiment No.	N/10 NaOH per 25 cc. saturated ester solution.	Molar solubility.
1	3.88	0.01552
2	3.96	0.01584
Average		0.01568

Any reaction between a difficultly soluble ester and a base will be monomolecular so long as conditions are such that the concentration of the ester is kept at the maximum allowed by its solubility. It is, of course, apparent that the solubility of the ester may be increased by the formation of alcohol in the reaction mixture. However, the error from this source in dilute solution is small.

In order to test the correctness of the value for K as found in Table I, the rate of saponification was determined in homogeneous aqueous solution by using a concentration not exceeding the maximum solubility of the ester. The values for K in this case were calculated according to the equation for a reaction of the second order $K = \dfrac{1}{t} \cdot \dfrac{x}{a\,(a-x)}$. The results are found in Table II.

TABLE II.—*Saponification of methyl benzoate with NaOH.*

NaOH = 0.0147. Ester = 0.0147. T = 30° ± 0.1°. Indicator corallin.

t.	x.	a — x.	$K=\frac{1}{t} \cdot \frac{x}{a\,(a-x)}$
0	0	0.0147	-----------------
5	0.0044	0.0103	5.784
10	0.0066	0.0081	5.516
16	0.0082	0.0065	5.345
26	0.0098	0.0049	5.232
36	0.0107	0.0040	5.055
46	0.0116	0.0031	5.534
Average ---------			5.411

The values for K obtained by the two methods agree fairly well in magnitude, considering that the small concentrations used, when working in homogeneous solution, greatly magnified the experimental error.

THE SAPONIFICATION OF THE METHYL ETHER OF METHYL SALICYLATE

The methyl ether of methyl salicylate was also investigated in the same manner to test the validity of calculating the reaction velocity constant in nonhomogeneous solution according to a reaction of the first order. The solubility of the methyl ether of methyl salicylate in water at 30° was first determined by the same method as was used for methyl benzoate. The results are:

Experiment No.	N/10 NaOH required for 25 cc. saturated solution of ester.	Molar solubility.
1-------------------------------- --------------	9.20	0.0368
2-------------------------------- -------------	9.32	0.0373
3---	9.30	0.0372
Average----------		0.0371

The data for the saponification of this ester with sodium hydroxide in nonhomogeneous and homogeneous solutions are found in Tables III and IV, respectively. Again the two methods of obtaining the reaction velocity constant give fairly satisfactory agreement.

TABLE III.—*Saponification of methyl ether of methyl salicylate with NaOH in nonhomogeneous sólution. NaOH = 0.1030. Ester (excess) = 0.371 constant. T = 30° ± 0.1. Indicator corallin.*

t.	x.	a—x.	$K_1 = \frac{2.3}{t} \cdot \log \frac{a}{a-x}$	$K = \frac{K_1}{0.0371}$
0	0	0.1030		
4	0.0270	0.0760	0.07590	2.046
9	0.0514	0.0516	0.07671	2.068
14	0.0690	0.0340	0.07909	2.131
20	0.0814	0.0216	0.07800	2.103
30	0.0921	0.0109	0.07479	2.016
40	0.0960	0.0070	0.06716	1.810
Average				2.029

TABLE IV.—*Saponification of the methyl ether of methyl salicylate with NaOH in homogeneous solution. NaOH = 0.0308. Ester = 0.0308. T = 30° ± 0.1. Indicator corallin.*

t.	x.	a—x.	$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$
0		0.0308	
4.5	0.0078	0.0230	2.447
9.0	0.0132	0.0176	2.706
15.0	0.0169	0.0139	2.631
25.0	0.0205	0.0103	2.585
35.0	0.0228	0.0080	2.643
45.0	0.0240	0.0068	2.547
55.0	0.0252	0.0056	2.655
75.0	0.0263	0.0045	2.530
Average			2.593

IV. THE EFFECT OF CONTACT ACTION

In order to determine the possible influence of contact action on the saponification, the rate of change in the presence of large excess of ester was compared with that in presence of small excess, methyl salicylate being employed for this purpose.

The theoretically equivalent amount of ester was shaken for about two hours with 25 cubic centimeters of N/10 sodium hydroxide solution, the shaking apparatus revolving at about 20

revolutions per minute. The ester in this case did not emulsify, but remained in one large globule, which at each revolution rolled from one end of the tube to the other.

A second experiment using five times the theoretical equivalent of ester was carried out simultaneously with hydroxide solution of the same strength and at the same temperature, 30°. These tubes were revolved at the rate of 120 revolutions per minute, which was sufficiently vigorous to break up the ester into fine globules which for the most part remained suspended in the aqueous solution. The following results were obtained on titration:

	Experiment No. 1. Equivalent amount of ester; 20 revolutions per minute.	Experiment No. 2. Five times the equivalent amount of ester; 120 revolutions per minute.
(a)	0.0278	0.0280
(b)	0.0280	0.0283
Average	0.0279	0.02815

While the amount transposed in experiment 1 was found to be slightly less, the difference is not greater than experimental error. Contact action is therefore excluded.

V. THE SAPONIFICATION OF METHYL SALICYLATE

When methyl salicylate is shaken with aqueous sodium hydroxide, there exist in solution the following substances, the concentrations of which are represented by the symbols following them: Free base (n), free ester (e), sodium methyl salicylate (m), di-sodium salicylate (d), and mono-sodium salicylate (s). If such a reaction mixture is titrated with a strong acid, using Congo red as an indicator, all the sodium which exists in the carboxyl group will be titrated as combined, while that existing as free base or substituted in the phenol group will be titrated as free.[15] That is, if a represents the total sodium and x the combined sodium,

$$x = s + d \qquad\qquad (3)$$
$$a - x = m + n + d. \qquad\qquad (4)$$

We have also established the relationships

$$\frac{en}{m} = r = 0.001 \qquad\qquad (1)$$

$$\frac{ns}{\delta} = r = 0.03 \qquad\qquad (3)$$

$$e = 0.005 \qquad\qquad (7)$$

[15] Poirrier blue is the only known indicator for the acidity of phenol. Imbert et Astruc, *Compt. rend. Acad. sci.* (1900), **130**, 35.

By solving algebraically the simultaneous equations: (1), (2), (3), (4), and (7), we may express n, the free base in our experiment, in terms of x as follows:

$$n = \frac{\sqrt{X^2 - ax + 0.018824} - (x + 0.0428)}{6}, \qquad (8)$$

in which $a = 0.0944$. (Table II.)

Now, when methyl salicylate is saponified, the rate of the reaction will be proportional to the product of the free base and the free ester; that is,

$$\frac{dx_1}{dt} = K \text{ en}, \qquad (9)$$

in which x_1 is the amount of ester hydrolysed and K is the reaction velocity constant.

However, upon consideration it will be apparent that this reaction is accompanied by another saponification reaction which results in the same products. For it is erroneous to suppose, as Goldschmidt does, that sodium methyl salicylate, $C_6H_4 \begin{smallmatrix} ONa \\ COOCH_3 \end{smallmatrix}$,
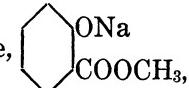
can exist in the presence of free NaOH without undergoing saponification, according to the equations

$C_6H_4 \cdot ONa \cdot COOCH_3 + NaOH \quad \rightarrow C_6H_4 \cdot ONa \cdot COONa + CH_3OH$

$C_6H_4 \cdot ONa \cdot COONa + H_2O \quad \leftrightarrows C_6H_4 \cdot OH \cdot COONa + NaOH.$
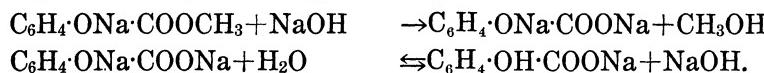
The rate at which this saponification takes place will in all probability be different from that at which the free ester is saponified. That this rate is appreciable cannot be doubted, since it is impossible to assign to the sodium in the phenol position *per se* the peculiar property of entirely protecting the adjacent —$COOCH_3$ group from attack. If x_2 is taken to represent the concentration of the substance transposed by this reaction, we can express the velocity of this saponification by the equation

$$\frac{dx_2}{dt} = K_1 m \, n, \qquad (10)$$

in which K_1 is the reaction velocity constant and $m \, n$ is the product of the concentrations of the reacting substances. But from (1) and (7), $m = 5n$. Substituting this value in (10), we obtain

$$\frac{dx_2}{dt} = K_1 \, 5n^2 \qquad (11).$$

Now, if x_1 represents the amount of free ester transformed, and x_2 the amount of sodium methyl ester transformed, their

sum will represent the total result of hydrolysis at any time t. This may be obtained experimentally by titration, and is the quantity which we have represented by the symbol x. The fact that x represents di-sodium salicylate as well as mono-sodium salicylate is of no moment in this connection since both are products of saponification. Then, if $x = x_1 + x_2$, $\dfrac{dx}{dt} = \dfrac{dx_1}{dt} + \dfrac{dx_2}{dt}$.

Adding (9) and (11),

$$\frac{dx}{dt} = K \, en + 5 \, K_1 \, n^2 \qquad (12).$$

Substituting in (12) the value 0.005 for e and the value of n obtained in (8), we have

$$\frac{dx}{dt} = \frac{0.005K}{0.6} \left[\sqrt{x^2 - 0.0944x + 0.018824} - x - 0.0428 \right]$$
$$+ \frac{5K_1}{36} \left[\sqrt{x^2 - 0.0944x + 0.018824} - x - 0.0428 \right]^{.2} \quad (13).$$

Let $K_2 = \dfrac{0.005K}{6}$ and $K_3 = \dfrac{5K_1}{36}$. Then $\dfrac{dx}{dt} =$

$K_2 \left[\sqrt{x^2 - 0.0944x + 0.018824} - x - 0.0428 \right] +$
$K_3 \left[\sqrt{x^2 - 0.0944x + 0.018824} - x - 0.0428 \right]^{2.}$ [16] $\qquad$ (I).

The integral of this differential equation is a very complicated expression containing the two constants in several different forms, and it would be extremely difficult to determine them from the integral expression after substitution of the experimental values for t and x in Table V. It is possible, however, to get approximate values for K_2 and K_3 by the application of Simpson's rule to the differential equation. The degree of approximation can afterwards be tested, and the values of the constants modified, if necessary.

In applying Simpson's rule in this case, the method of procedure is as follows:

Putting the equation into the form of a definite integral

$$\int_{t_1}^{t_2} dt = \int_{X_1}^{X_2} \frac{dx}{K_2 \, [Z] + K_3 \, [Z]^2,} \qquad (II).$$

we see that the time t is the area under the curve plotted between values of x as abscissas and the values of $\dfrac{1}{K_2 \, [Z] + K_3 \, [Z]^2}$ as ordinates.

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[16] In the following equations, the term inside the brackets will be expressed by Z for the sake of brevity.

Taking different intervals of time from the experimental data in Table V, we can form as many independent equations as we please. Six different intervals were taken; namely,
$t = 600 - 65 = 535$ min., $t = 540 - 65 = 475$ min., $t = 480 - 65 = 415$ min., $t = 600 - 185 = 415$ min., $t = 600 - 245 = 335$ min., and $t = 600 - 305 = 295$ min.

The differences between the corresponding values of x were divided into 10 equal parts and the values of $\dfrac{1}{K_2\,[Z] + K_3\,[Z]^2}$ computed. For example, the equation for $t = 535$ min. is

$$\int_{65}^{600} dt = 535 = \frac{0.00598}{3}[(Y_0 + Y_{10}) + 2(Y_2 + Y_4 + Y_6 + Y_8)$$

$$+ 4(Y_1 + Y_3 + Y_5 + Y_7 + Y_9)]$$

The values of y_0, y_1, etc., are $\dfrac{1}{K_2\,(0.0613) + K_3\,(0.00376)}$ $\dfrac{1}{K_2\,(0.054) + K_3\,(0.00292)}$, etc.

In summing up the values of y, the denominator was factored in such a way as to make one factor the same as the numerator and the other containing K_2 and K_3 to the first power. Of course, factoring exactly is impossible, but the difference between the numerator and the first factor of the denominator was very small and canceling them with each other allowable. To illustrate:

$$t = 475 = \frac{0.00567}{3}\left[\frac{1}{K_2\,(0.0008067) + K_3\,(0.00001398)}\right], \quad (14)$$

$$t = 415 = \frac{0.00543}{3}\left[\frac{1}{K_2\,(0.000877 + K_3\,(0.0000178)}\right]. \quad (15)$$

Solving for K_2 and K_3 between these equations

$$K_2 = 0.00454, \quad K_3 = 0.0223.$$

Proceeding in this way with the other equations, a set of values of K_2 and K_3 may be determined.

Since in the expression for y the effect of K_3 is very small compared with that of K_2, K_3 being multiplied by the square of the coefficient of K_2, a small quantity in itself, we are justified in assuming its value as correct and substituting it in the four other equations to determine K_2.

The four remaining equations are:

$$t = 535 = \frac{0.00598}{3} \left[\frac{1}{K_2 \, (0.000704) + K_3 \, 0.0000097} \right], \quad (16)$$

$$t = 415 = \frac{0.00345}{3} \left[\frac{1}{K_2 \, (0.0005095) + K_3 \, (0.000005975)} \right], \quad (17)$$

$$t = 335 = \frac{0.00252}{3} \left[\frac{1}{K_2 \, (0.0004309) + K_3 \, (0.00000438)} \right], \quad (18)$$

$$t = 295 = \frac{0.00191}{3} \left[\frac{1}{K_2 \, (0.000378) + K_3 \, (0.00000374)} \right], \quad (19)$$
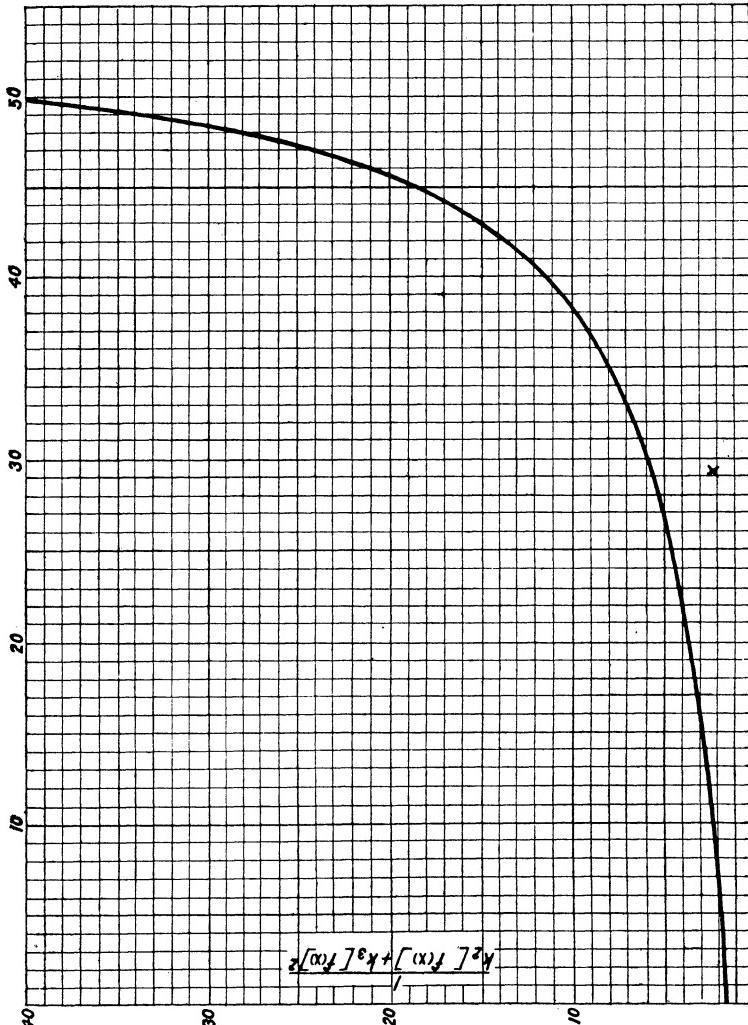

FIG. 2.—A curve for the graphic determination of t, to test the accuracy of the values: $K_2 = 0.0053$; $K = 6.36$; $K_3 = 0.0223$; $K_1 = 0.1605$.

Substituting 0.0223 for K_3 in (16), (17), (18), and (19), we obtain, for K_2, 0.00498, 0.005176, 0.005589, and 0.005489, respectively. The mean of the five values of K is 0.00516.

Now, putting $t_2=600$, $t_1=305$, $x_2=0.0861$, and $x_1=0.067$ in equation II and applying Simpson's rule, we get $t=311.47$ minutes instead of 295 minutes, the observed value. Leaving K_3 as it is and changing K_2 to 0.0053, we obtain for the same difference between the values of x, 303.6 minutes, an error of 2.5 per cent.

Plotting the values of x as abscissas and the values of

$$\frac{1}{K_2[Z]+K_3[Z]^2}$$ as ordinates, using $K_3=0.0223$ and $K_2=0.0053$,

we obtain a smooth curve, which shows that the values of K_2 and K_3 are at least very good approximations (fig. 2). We can now test the accuracy of the constants by computing the values of t from the area under this curve. For example, the area under the curve from $x=0.0516$ to $x=0.0861$ gives 400.54 minutes instead of 415 minutes, an error of 3.5 per cent.

Similarly, values of t computed from the curve between different values of x agree well with the observed values of t, except for the first three values of x. The values of t from $x=0.04$ and $x=0.069$, for instance, show a discrepancy of 25 per cent.

This greater discrepancy during the earlier part of the saponification is undoubtedly due to the excessive velocity of the transformation as compared with the rate of solution.

TABLE V.—*Saponification of methyl salicylate with NaOH 0.0944 Normal.*
T=30° ± 0.1.   Congo red indicator.

t.	x	a—x.	$\overline{K}_{mono}$.	t (inter-polated values).	K_2, (when K_3=0.0223).
0	0	0.0944	0.00218		
65	0.0263	0.0681	0.00194		
125	0.0400	0.0544	0.00186		
185	0.0516	0.0428	0.00184		
245	0.0609	0.0335	0.00176		
305	0.0670	0.0274	0.00176	295	0.005489
365	0.0721	0.0223	0.00176	335	0.005589
415	0.0769	0.0175	0.00174	415	0.005176
480	0.0806	0.0138	0.00168	475	0.004540
540	0.0830	0.0114	0.00176	535	0.004980
600	0.0861	0.0083			
				Mean ___	0.005160

If we take the values $K_2=0.0053$ and $K_3=0.0223$, $K=6.36$ and $K_1=0.1605$. This value of K agrees very well with the value calculated by Goldschmidt. His whole calculations, however, ignore the possibility of any saponification of sodium methyl salicylate taking place. While such a supposition was not justified by any facts at his command, yet it proved to be nearly true. That is, the reaction velocity constant of the saponification of sodium methyl salicylate proves to be only about 0.1605 or about 1/40 of that of methyl salicylate. His error, therefore, did not prove great enough to invalidate his mean numerical value for $K\chi$, although the constancy of his values left much to be desired.

It is rather startling to find that sodium methyl salicylate is saponified so extremely slowly as compared with the free ester. In the following paper,[17] an investigation is described which throws some light upon these facts.

VI. HYDROLYSIS OF METHYL SALICYLATE WITH SODIUM CARBONATE

Methyl salicylate was saponified with a pure, freshly prepared solution of 0.3998 normal sodium carbonate. The temperature
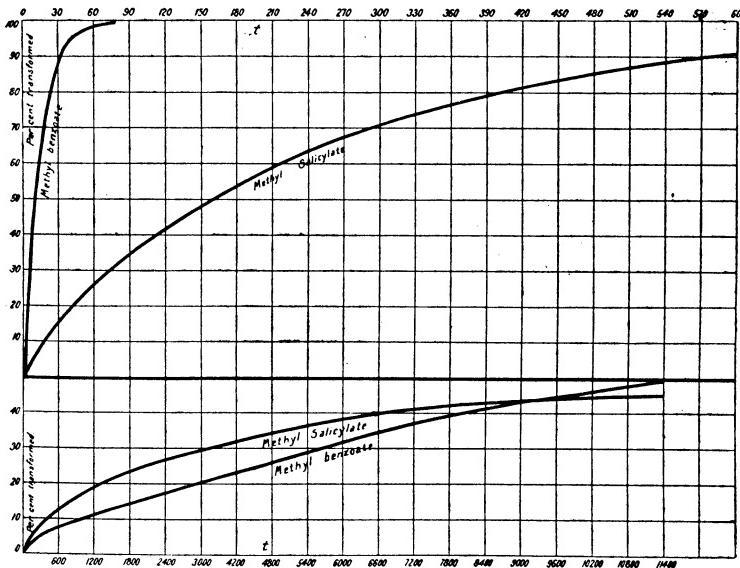

FIG. 3.—Saponification of methyl salicylate and benzoate with NaOH (above) and Na_2CO_3.

[17] Gibbs and Pratt, *This Journal, Sec. A* (1913), **8**, 33.

was kept at 25°. Saponification, with a large excess of the ester, was carried on in small bottles filled to the neck with the standard solution. A separate bottle was used for each titration, and all were kept tightly stoppered with glass stoppers until titrated. By this means no carbon dioxide was allowed to escape. Under these conditions it is theoretically possible to calculate the concentration of the free base and the velocity constants, but the complexity of the mathematical treatment necessary is such as to render it impractical. The experimental data are given in Table VI for purposes of comparison with Table VII, which contains the same data for methyl benzoate. It will be seen that a similar relationship exists between the rates of saponification of methyl benzoate and methyl salicylate, whether sodium hydroxide or carbonate is used for saponification (fig. 3). Saponification practically ceases when all the carbonate has been converted into the bicarbonate.

TABLE VI.—$T=25°\pm0.1$.   *Methyl salicylate=excess.* $Na_2CO_3=0.3998$ $N.$

$\frac{t}{60}$	x.	a—x.	1000 K$_{mono.}$
1	0.0130	0.3868	0.240
3	0.0250	0.3748	0.155
5	0.0334	0,3664	0.126
8	0.0467	0,3531	0.112
12	0.0572	0.3426	0.093
20	0.0777	0.3221	0.079
30	0.0919	0.3079	0.063
50	0.1180	0.2880	0.047
100	0.1539	0.2459	0.035
190	0.1797	0.2201	0.023

TABLE VII.—*Methyl benzoate=excess.* $Na_2CO_3=0.3998$ $N.$ $T=25°\pm0.1.$

$\frac{t}{60}$	x.	a—x.	1000 K$_{mono.}$
1	0.0098	0.3900	0.180
3	0.0145	0.3853	0.090
5	0.0215	0.3783	0.080
8	0.0305	0.3693	0.072
12	0.0335	0.3663	0.053
20	0.0394	0.3604	0.035
30	0.0450	0.3548	0.029
50	0.0748	0.3250	0.027
100	0.1267	0.2731	0.027
190	0.1982	0.2016	0.026

VII. THE HYDROLYSIS OF METHYL SALICYLATE IN WATER

MEASUREMENTS AT 30°

The methyl salicylate employed was especially purified by shaking with sodium hydrogen carbonate solution, drying over fused calcium chloride, and distilling at 6 millimeters' pressure.

A few determinations carried on without precautions to insure great accuracy showed that saturated solutions of salicylic acid in water and in methyl salicylate contained at 30° about 0.32 gram per 100 cubic centimeters of the former solvent and 9.81 grams in the latter, a ratio of about 1 to 30 or 31. Saturated aqueous solutions of salicylic acid shaken with methyl salicylate until equilibrium was reached have the following distribution of salicylic acid.

One volume water and one-half volume methyl salicylate gave 6 per cent of the salicylic acid in the water and 94 per cent in the ester as the average of a number of determinations.

One volume of water and one volume of ester gave about 3 per cent in the water and 97 per cent in the ester, a ratio of about 1 to 32.

Conductivity measurements.—Conductivity measurements were made at 30° in small cells in one end of which the electrodes were sealed (fig. 4). After the introduction of the solution, the other end was sealed.
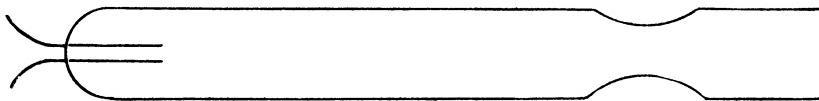
FIG. 4.—Conductivity cell.

The cells were standardized at 30° by means of N/50 potassium chloride solution, and the data given in Kohlrausch and Holborn [17] and the Kohlrausch methods and standards were employed in the manipulation.

It is realized that measurements at 30° introduce some complications, but at lower temperature a serious error was sometimes encountered, because of the construction of the cell which permitted a short circuit at the point where the electrodes were sealed into the glass due to the condensation of moisture from the humid atmosphere of this locality.

The first conductivity measurements, recorded in Table VIII, were made in a cell charged with 15 cubic centimeters of water

[17] Das Leitvermögen der Elektrolyte. Leipzig (1898).

and 0.5 cubic centimeter of methyl salicylate. While the conductivity of the aqueous solution of methyl salicylate can be estimated in this experiment, it is obviously impossible to follow the hydrolysis with any degree of accuracy, for the reason that a considerable proportion of salicylic acid is removed from the aqueous solution by the methyl salicylate.

The first measurement, t_o, was made after vigorously shaking together the methyl salicylate and the water for one-half minute. The tube was then placed on a revolving wheel and agitated continuously between successive observations.

In the following table, t is the time in minutes; R, the resistance in ohms; ζ the dilution, that is, the number of liters containing a gram molecule; Λ, the molecular conductivity; a, the degree of dissociation; and K_A, the affinity constant of the methyl ester of salicylic acid.

TABLE VIII.—*Conductivity of methyl salicylate in aqueous solution.*

Cell No. 1.   Constant $= 0.1549$.   Temperature $= 30°$.

$\dfrac{t}{60}.$	$R =$ ohms.	$\zeta \cdot 10^{-3}.$	$\Lambda.$	$a.$	$K_A.$
0	17,040	200	0.80	0.00212	$2.2 \cdot 10^{-11}$
116	16,360	200	0.91	0.00247	$2.9 \cdot 10^{-11}$
193	13,400				
235	12,200				
284	11,900				
331	10,900				
649	8,100				

At this time, the cell was placed on an open steam bath to hasten the action, and at $\dfrac{t}{60} = 1768$ the resistence had dropped to 355 ohms, a point approaching equilibrium.

The tube was opened, and the contents analyzed as follows:

Water solution, 15 cubic centimeters.

Substance.	Amount in 100 cc.
Methyl salicylate	0.0927
Salicylic acid (almost all present as salt)	0.0792
Methyl alcohol	0.0181

Methyl salicylate solution, 0.5 cubic centimeter in volume.

| Salicylic acid | * 0.272 |

* This determination is perhaps not very accurate.

In order to avoid some of the difficulties experienced in the first experiment, a second cell was constructed of glass which

was more resistant to the solvent action of acids, and the amount of methyl salicylate was so reduced that the quantity of salicylic acid which it would remove from the water would be negligible. The temperature was maintained at approximately 30° throughout the experiment.

The cell was charged with 15 cubic centimeters of water and 2 drops of pure methyl salicylate and then carefully sealed. A very small quantity of the ester remained undissolved.

The first reading, t_0 was made after shaking the cell vigorously for one-half minute. In Table IX, the data given are:

Column 1. t = time in minutes.
    2. The resistance of the cell in ohms.
    3. The concentration of the ester taking the molar solubility as 0.005.
    4. The molecular conductivity of the ester corrected for the conductivity of the water.
    5. The degree of dissociation of the ester, $\Lambda \infty = 386$.
    6. The affinity constant (K_A) of the ester calculated from the preceding data.
    7. K, the specific conductivity, as calculated from the resistance capacity of the cell and the data in column 2.
    8. The concentration of the salicylic acid estimated, from K in column 7, upon a curve plotted from values calculated from the data in Kohlrausch and Holborn.
    9. The molar concentration of the salicylic acid calculated from data in column 8. This value is also X, the amount of methyl salicylate hydrolyzed in time t.
    10. The molecular conductivity of the salicylic acid solution calculated from the data in columns 2 and 8 and the resistance capacity of the cell and not corrected for the conductivity of the water and the methyl salicylate in solution. These values give some idea of the accuracy of the work.
    11. K_H is the velocity constant for the reaction $C_6H_4{<}^{OH}_{COOCH_3}$ $+H_2O$

$$= C_6H_4{<}^{OH}_{COOH} + CH_3OH$$ calculated from $dx/dt = K_H e$ in which the constant $e = 0.005$, the solubility of methyl salicylate in water at 30°. Therefore $K_H = \frac{x}{et}$.

While the values for e are constant, limited by the solubility of the methyl salicylate, it seems more accurate to regard e as a variable which, as it diminishes, is regularly increased by another variable so that at each interval of time it assumes the same value.

TABLE IX.—*Conductivity data for methyl salicylate, the dissociation in aqueous solution, and the rate of hydrolysis. First series.*

Cell No. 2.   Constant = 0.1670.   Temperature 30°.

1	2	3	4	5	6	7	8	9	10	11
$\frac{t}{60}$	$R =$ ohms.	$\int \cdot 10^{-3}$ for ester.	Λ for ester.	α for ester.	K_A for ester.	$K = \frac{C \cdot 10^4}{R}$	$\int \cdot 10^{-3}$ for salicylic acid.	x.	Λ for salicylic acid.	$K_H = \frac{x}{et}$.
0	27,900	200	0.217	0.00057	$1.7 \cdot 10^{-11}$					
3	21,900	200	0.55	0.0014	$1.0 \cdot 10^{-11}$					
5.5	20,000	200	0.69	0.0018	$1.6 \cdot 10^{-11}$					
22	15,200	200	1.22	0.0032	$5.1 \cdot 10^{-11}$					
25.5	14,400					0.116				
45	12,900					0.129	29,900	0.04334	[a] (387)	
363	6,100					0.274	14,500	0.04689	397.1	$6.3 \cdot 10^{-7}$
407	5,895					0.283	13,900	0.04720	393.8	$5.9 \cdot 10^{-7}$
454	5,495					0.304	13,200	0.04758	401.1	$5.6 \cdot 10^{-7}$
549	5,200					0.321	12,500	0.04800	401.6	$4.9 \cdot 10^{-7}$
607	4,980					0.335	11,900	0.04841	399.0	$4.7 \cdot 10^{-7}$
842	3,780					0.442	8,900	0.0_31124	393.2	$4.4 \cdot 10^{-7}$
1,053	3,520					0.475	8,100	0.0_31245	384.4	$3.9 \cdot 10^{-7}$
1,269	3,180					0.525	7,300	0.0_31370	382.5	$3.6 \cdot 10^{-7}$
Average										$4.9 \cdot 10^{-7}$

[a] Value at infinite dilution = $\Lambda \infty$.

The hydrolysis was continued for twenty-three days longer, but the changes in the resistance of the solution were so uncertain, undoubtedly due to the action upon the glass, that the experiment was discontinued.

Analysis of the contents of tube.

Compound.	Calculated to 100 cc.
Methyl salicylate	0.0739
Salicylic acid	0.0048

The percentage of methyl salicylate is slightly less than the solubility, and the amount of salicylic acid formed from the methyl salicylate at the end of twenty-three days is about two and one-half times the quantity shown by the conductivity at the expiration of twelve hundred sixty-nine hours.

The results of a duplicate experiment performed in a third cell are recorded in Table X.

TABLE X.—*The hydrolysis of methyl salicylate in aqueous solution. Second series.*[a]

Cell No. 3. Constant = 0.1761. Temperature 30°.

1	2	7	8	9	11
$\dfrac{t}{60}$	R.	K = C/R.	$\zeta \cdot 10^3$ salicylic acid.	X methyl salicylate.	$K_H = \dfrac{x}{et}$
70	11,000	0.0$_3$01601	-----------	-----------	-----------
117	7,800	0.0$_3$02257	17,000	0.0$_3$0588	-----------
429	6,700	0.0$_3$02628	14,700	0.0$_3$0680	5.3·10—7
669	6,100	0.0$_3$02887	13,700	0.0$_3$0730	3.6·10—7
934	4,300	0.0$_3$04095	9,600	0.0$_3$1042	3.7·10—7
1,346	2,900	0.0$_3$06072	6,400	0.0$_3$1563	3.9·10—7
1,896	1,970	0.0$_3$08938	4,100	0.0$_2$2439	4.3·10—7
2,926	1,150	0.0$_3$15310	2,200	0.0$_3$4546	5.2·10—7
Average					4.3·10—7

[a] The column numbers correspond to those in Table IX.

Great accuracy cannot be claimed for K_H for the reasons that the action of the solution upon the glass and the method employed for estimating the concentrations in column 8 will introduce unavoidable errors. The corrections for the conductivity of the water and that of the dissolved methyl salicylate are slight and have less influence than the former causes for inaccuracy. Slight changes in the temperature for such a long period of time were unavoidable, and the high temperature coefficient, which will be shown later to be one of the factors of this reaction, introduces a considerable source of error. On the whole, the approximation of K_H is very satisfactory under the circumstances, and the decreasing values may be due to the action upon the glass which is greatest at the beginning.

The value of K_A, the affinity constant of the methyl ester of salicylic acid, is problematical and is about the magnitude 10^{-11}. Calculated from the hydrolysis constant of the sodium salt, 0.001, as previously determined, the value is

$$\frac{1 \cdot 2 = 10^{-14}}{10^{-3}} = K = 1.2 \cdot 10^{-11}.$$

This value practically agrees with that obtained after shaking the ester with water for three or four hours.

Goldschmidt and Scholz's statements that the hydrolytic constant of sodium methyl salicylate, 0.001, is considerably larger than that of sodium phenylate, that the acid character of the

phenol is greatly weakened by the introduction of the $COOCH_3$ group in the ortho position, and that the affinity constant of the ester is probably one-tenth that of phenol are essentially correct.

Naumann, Müller, and Lantelme [18] have determined by the distillation method the percentage of hydrolysis of sodium phenylate at 100°, and the hydrolysis constant calculated from their values gives about the average $1.5 \cdot 10^{-3}$. It is possible that at 30° the temperature coefficient will reduce this figure to less than one-tenth of its value, in agreement with that given by Walker; [19] namely, $0.85 \cdot 10^{-4}$ at 25°.

Since the solubility of this ester at 100° was required in the study of the hydrolysis at this temperature, it was determined as follows:

One liter of pure water was boiled for thirty minutes with an excess of methyl salicylate. The ebullition was stopped and the ester then almost entirely settled to the bottom, leaving a small quantity floating. Small samples were syphoned into small weighed flasks, neutralized, and then saponified for two and one-half to three hours and titrated, employing phenolphthalein as indicator. The results are tabulated as follows:

TABLE XI.—*The solubility of methyl salicylate in water at 100°.*

Weight of sample.	N/10 NaOH required.	Ester in solution.	Molar solubility=e. Average.
Grams.		*Per cent.*	
61.19	7.06	0.1754	
60.94	6.48	0.1615	
53.20	7.45	0.2128	0.0117
51.96	5.60	0.1638	

MEASUREMENTS AT 100°

The hydrolysis was carried on in small flasks fitted with return condensers. Small quantities of methyl salicylate were from time to time added to the boiling solution, in order to avoid the presence of great excesses of the ester which would interfere with the accurate determination of the salicylic acid in the aqueous solution. Small quantities of the water solution were removed at intervals, and the salicylic acid determined by the colorimetric method.

[18] *Journ. f. prakt. Chem.* (1907), n. s. **75**, 68.
[19] Introduction to Physical Chemistry. London (1910), 36.

The results are recorded in Table XII. t is the time in minutes; x is the amount of methyl salicylate, expressed as molar concentration, hydrolyzed in time t; K_H is the reaction velocity constant calculated from the formula $K_H = \dfrac{x}{et}$. The value for e is taken as 0.0117.

TABLE XII.—*The hydrolysis of methyl salicylate at 100°.*

1	2	3	4
$\dfrac{t}{60}$	Salicylic acid in 100 cubic centimeters.	X.	$K_H = \dfrac{x}{et}$
1	0.00255	0.000185	$2.7 \cdot 10^{-4}$
2	0.00637	0.000462	$3.3 \cdot 10^{-4}$
5	0.02146	0.001555	$4.4 \cdot 10^{-4}$
7	0.02416	0.001751	$3.5 \cdot 10^{-4}$
24	0.11716	0.008492	$5.0 \cdot 10^{-4}$
30	0.12264	0.008884	$4.2 \cdot 10^{-4}$
48	0.19320	0.01400	$4.2 \cdot 10^{-4}$
72	0.21470	0.01556	$3.9 \cdot 10^{-4}$
96	0.25760	0.01867	$2.8 \cdot 10^{-4}$
120	0.32200	0.02333	$2.8 \cdot 10^{-4}$
168	0.38640	0.02800	$2.7 \cdot 10^{-4}$
Average			$3.6 \cdot 10^{-4}$

It is to be noted that about one thousand times the quantity of methyl salicylate is hydrolyzed in a given time at 100° as at 30°, an extremely high temperature coefficient.

The hydrolysis in N/10 solutions of sulphuric acid measured in the same manner in one experiment showed that the rate was considerably more rapid. Since the measurements have not been repeated, we are not justified in making any further statements.

Attempts were made to follow the rate of hydrolysis at 100° in sealed tubes fitted with electrodes by means of conductivity measurements, but the glass employed was so readily attacked that the measurements were of no significance. While the results are not satisfactory for the purposes in view, they may be of some interest and are briefly described as follows:

Sealed tubes containing equal quantities of methyl salicylate and conductivity water were agitated in a steam bath at 100° from October 7, 1908, to December 2, 1908—a period of fifty-six days—and the contents roughly estimated. Determinations are calculated to 100 cubic centimeters of solution.

Substances.	Methyl salicylate portion.		Aqueous portion.	
	Tube No. 1.	Tube No. 2.	Tube No. 1.	Tube No. 2.
Salicylic acid _____	0.497	0.51	trace	trace
Sodium salicylate_____	none	none	_____	0.69

The following experiments were more carefully performed. Tubes 1 and 2, of the shape shown in fig. 5, were constructed with platinized platinum electrodes.
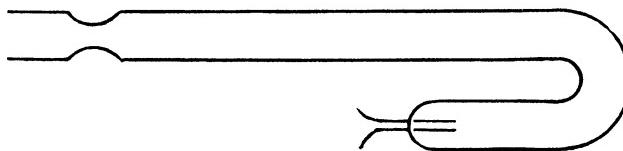

FIG. 5.—Conductivity cell.

The cell constants at 30° were: No. 1, 0.1913; and No. 2, 0.2158 Kohlrausch units.

Equal quantities of water and methyl salicylate were sealed in the tubes. The water employed had a specific conductivity of 1.9 10^{-6}. The U-shape of the cell permitted pouring the water from the elongated leg into the leg containing the electrodes, where its conductivity could be measured.

The two cells were put into a steam bath, which remained constant between 99° and 100°, and continuously rotated for three hundred seventy-two hours for cell 1 and seven hundred ninety hours for cell 2. At intervals, cell 1 was cooled to 30° and the resistance measured. This cell broke after three hundred eighty-four hours.

The resistances measured at intervals were as follows; temperature during measurements, 30°.

TABLE XIII.—*Resistance of cells during hydrolysis in water at 100°.*

Time.	R.	
	Cell No. 1, 5 cc. water 5 cc. ester.	Cell No. 2, 10 cc. water 10 cc. ester.
H. *m.*		
0 0	2,800	_____
3 15	640	_____
22 45	184	_____
46 45	122	_____
93 45	77	_____
128 15	70	_____
205 15	52	_____
272 15	45	_____
372 15	40	_____
_____	tube broken	_____
790 0	_____	38

It is evident that equilibrium was practically established in about four hundred hours.

Cell 2 was opened and analyzed after seven hundred ninety hours at 100°. It showed no internal pressure. The analysis is as follows:

Aqueous portion.

Substance.	Gram per 100 cc.
Free acid, calculated as salicylic	0.0055
Total salicylic acid	0.96
Methyl alcohol (by calculation)	0.307
Methyl salicylate	0.074

Almost all of the salicylic acid in the aqueous portion was present as alkali salts due to the action upon the glass.

Methyl salicylate portion.

Salicylic acid	0.425 gram per 100 cc.

The total amount of salicylic acid produced was 1.385 grams per 100 cubic centimeters, which is equivalent to 1.526 grams of methyl salicylate hydrolyzed.

Method of analysis.—The two layers, water and methyl salicylate, were separated and filtered. The salicylic acid in the ester portion was titrated with N/50 sodium hydrogen carbonate solution, employing Congo red as an indicator. The acidity of the aqueous layer was determined in the same manner. The total salicylic acid in the aqueous portion was determined as follows: An aliquot part was made alkaline with sodium hydrogen carbonate and then shaken out repeatedly with chloroform to remove dissolved ester. It was then acidified with sulphuric acid, and the salicylic acid extracted with chloroform and determined colorimetrically. The methyl salicylate in the aqueous solution was determined colorimetrically by the method previously described.[20]

Aliquot parts of the aqueous solution were gently ignited, and the alkali carbonates determined by titration.

SUMMARY

The results of the investigation of the saponification of some difficultly soluble esters with sodium hydroxide, and with pure water, in homogeneous and nonhomogeneous solutions and the mathematical considerations involved are described.

1. Carbon dioxide is found in small amounts as the result of the alkaline, but not of the acid hydrolysis of methyl salicylate

[20] Gibbs, *This Journal*, Sec. A (1908), 3, 357.

at room temperatures. The amount is so small that it is negligible in the consideration of the rate of saponification.

2. The constant for the hydrolytic dissociation of sodium methyl salicylate is about 0.001, which is the value given by Goldschmidt.

3. The solubilities of methyl benzoate and the methyl ether of methyl salicylate in water at 30° are 0.01568 and 0.0371, respectively. The solubilities of methyl salicylate in water at 30° and 100° are 0.005 and 0.0117, respectively.

4. The saponification constants for methyl benzoate and the methyl ether of methyl salicylate in homogeneous solution calculated according to the equation for reactions of the second order are 5.411 and 2.593, respectively. In nonhomogeneous solution, calculated according to the equation for reactions of the first order, they are 4.529 and 2.029, respectively; therefore, the saponification constants of difficulty soluble esters can be approximated by the second method.

5. The rate of saponification of a difficultly soluble ester, when the ester is present in excess of its solubility, is not affected by contact action.

6. The saponification velocity constant of methyl salicylate with sodium hydroxide in nonhomogeneous solution was determined to be 6.36, and that of sodium methyl salicylate was found to be 0.1605.

7. The saponification of methyl benzoate and methyl salicylate in sodium carbonate solution has been studied for purposes of comparison with the above data.

8. The affinity constant of methyl salicylate calculated from the conductivity measurements at 30° is of the magnitude 10^{-11}. This value agrees with that calculated from the hydrolysis constant of the sodium salt.

9. The hydrolysis of methyl salicylate in pure water at 30° and 100° has been investigated by measurements of the conductivity of the solutions. At 30° the rate is $4.6 \cdot 10^{-7}$; and at 100°, $3.6 \cdot 10^{-4}$.

ILLUSTRATIONS
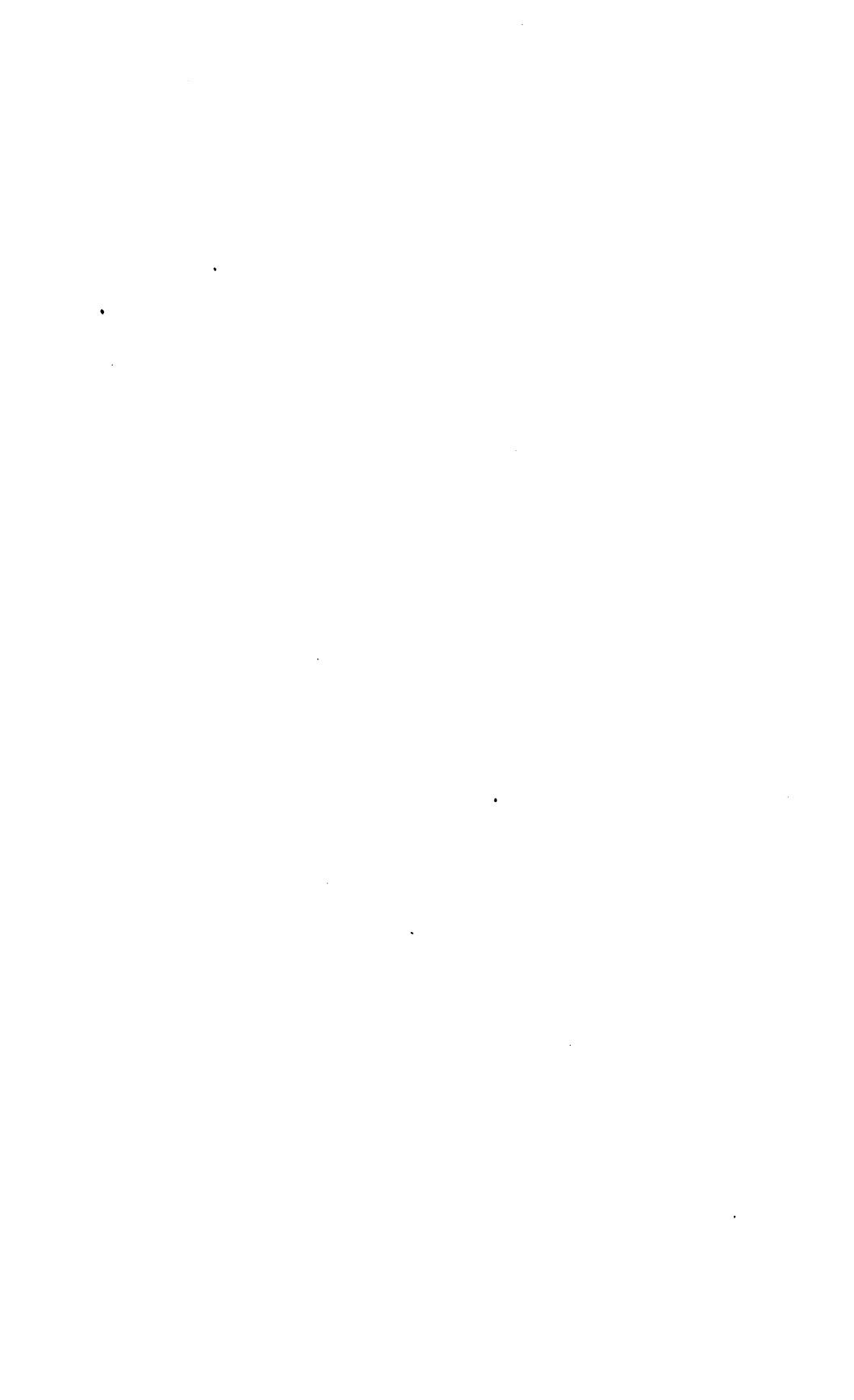
THE MUTUAL INFLUENCE OF HYDROXYL AND CARBOXYL AND SOME RELATED GROUPS IN THE ORTHO POSITION

A STUDY OF THE ABSORPTION SPECTRA OF PHENOL, O-CRESOL, O-HYDROXY-BENZYL ALCOHOL, SALICYLIC ACID AND ITS METHYL ESTER, METHYL ETHER OF SALICYLIC ACID AND ITS METHYL ESTER, BENZYL ALCOHOL, BENZYL ACETATE, BENZYL METHYL ETHER, BENZYL CHLORIDE, AND METHYL BENZOATE

By H. D. GIBBS [1] and D. S. PRATT

(*From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.*)

Five text figures

The following investigation was undertaken with the view of throwing some light upon the behavior of the compounds which exist in solution during the saponification of methyl salicylate described in the previous paper.[2]

If it be true that the strengths of carboxylic acids are determined by the reactivity of the carboxylic $>C=O$ group, it should be possible to compare spectroscopically certain analogous acids which show ultra-violet absorption bands. Baly and Schaefer [3] state:

There are thus two influences at work which determine the affinity of the carbonyl group in carboxylic acids, namely, (1) the nature of the adjacent carbon atom, and (2) the condition of the hydroxylic oxygen.

It is to be expected that these influences would change the relative position and persistence of ultra-violet absorption bands, and that a study of a series of closely related compounds in which they are varied, both collectively and separately, would result in a clearer understanding of the chemical and physical behavior of the compounds in solution.

The astonishingly great difference between the saponification rates of methyl salicylate and its sodium salt (6.63 and 0.161, respectively) must be due to a decreased activity of the carbonyl which in this case is attributed to a change in the equilibrium of forces between this group and the hydroxyl group in the ortho position.

115512——3

The analogies existing between methyl salicylate and aceto-acetic ether are very striking. The chemical relationships have been pointed out by Freer,[4] and determinations of the affinity constants of the acids and the hydrolysis constants of their sodium salts show the former to be of the magnitude 10^{-11} and the latter 0.001 in each case.

The expressions suggested by Hantzsch [5] for the valence isom-

erism in the *aci-salt* in explanation of the absorption band in acetoacetic ether can be applied to methyl salicylate, the corresponding form showing the conjugated linking being:
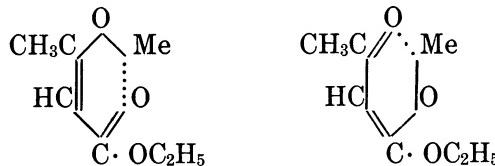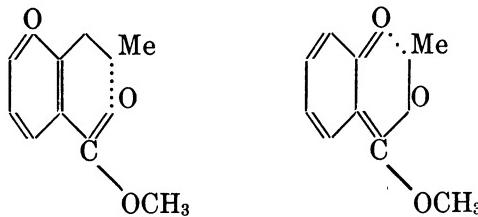
There is no doubt that methyl salicylate in the presence of alkali behaves very differently from the other phenolic compounds discussed in this paper.

Phenol, *o*-cresol, salicylate acid, and *o*-hydroxybenzyl alcohol in the presence of alkali show a reduction in the persistence of the characteristic absorption band (discussed later), while aceto-acetic ether shows no band in the absence of alkali, but develops a characteristic band which increases in persistence with the increasing concentration of alkali salt. Methyl salicylate shows no appreciable change in the persistence of its band with alkali, the effect of increasing concentration of the latter being to shift the band toward the red. If the intramolecular vibration producing this band is to be attributed to the conjugated linking as above represented, it is clear that an excess of alkali has

[4] *Am. Chem. Journ.* (1892), **14**, 407.
[5] *Ber. d. deutschen chem. Ges.* (1910), **43**, 3053.

a beneficial rather than a prejudicial action. The effect of the alkali is to reduce the phenolic condition, which we will show can be practically eliminated.

This is actually the case in phenol, *o*-cresol, *o*-hydroxybenzyl alcohol, and sodium salicylate. The primary effect of the alkali upon salicylic acid is the formation of the sodium salt, and this is manifested in the absorption spectrum by a shift of the band toward the shorter wave length, a position nearer the characteristic band of phenol.

It is evident that the carboxylic C=O group has not the effect in the di-sodium salt of salicylic acid that it has in the sodium salt of the ester.

The above representation for sodium methyl salicylate indicates that the free affinities of this compound are so bound that in effect its equilibrium more closely resembles that of an ether than of an ester. By this assumption the greatly decreased rate of saponification of sodium methyl salicylate is capable of explanation. Salicylic acid, on the other hand, shows no similar behavior in the presence of alkalies, and presents no corresponding analogies to acetoacetic ether, although the absorption spectra of the free acid and ester are identical. When methyl is employed instead of sodium to replace the hydroxylic hydrogen of methyl salicylate forming the methyl ether of methyl salicylate, the equilibrium is disturbed in a different manner due to the fixation of the labile hydrogen atom, and this is manifested by a shift in the absorption band toward the shorter wave lengths and a decrease in its persistence, indicating decreased activity. This decreased activity cannot be attributed to the phenol portion of the molecule, for the absorption spectrum of phenol is not altered in this way by its change to anisole, but is due to the reduction of the influence upon the $>C=O$ group.

The strength of salicylic acid is diminished by the change of the hydroxyl group to methoxyl. This is shown in the absorption spectra of these compounds by a decided shift in the absorption band of the former toward the shorter wave lengths. The absorption bands of neither of these compounds are altered by the change of the carbonyl group to its methyl ester. It is evident that the strength of the acid is affected by any neighboring group which will influence the potential activity of the. $>C=O$ group of the carboxyl. The absorption spectra of salicylic acid, methyl ether of salicylic acid, and benzoic acid indicate the strength of these acids to be in the order named, a fact which is in accord with their affinity constants.

The rates of saponification of the methyl esters of the above-mentioned acids and the affinity constants of these acids are tabulated as follows:

Acid.	Rate of saponi-fication of the methyl ester.	Affinity constant.[a]
Salicylic acid	6.36	0.104
Methyl ether of salicylic acid	[b]2.03–[c]2.60	0.0081
Benzoic acid	[b]4.53–[c]5.41	0.0067

[a] The affinity constants are taken from Derick, *Journ. Am. Chem. Soc.* (1912), **34**, 76; Lunden, "Affinitätsmessungen an schwachen Säuren und Basen," Sammlung chem. u. chem-tech. Vorträge (1909), **14**, 1; and Ostwald, *Zeitschr. f. physik. Chem.* (1889), **3**, 241.

[b] Calculated for reaction of the first order in nonhomogeneous solution.

[c] Calculated for reaction of the second order in homogenous solution.

These values show that the affinity constants are not in the same order as the saponification constants. Similar irregularities are shown in the values as given for propionic, butyric, and isobutyric acids.

Acid.	Rate of saponi-fication of the ethyl-ester.[a]	Affinity constant.[a]
Propionic	2.186	0.00145
Butyric	1.702	0.00175
Isobutyric	1.731	0.00159

[a] Values taken from Walker, Introduction to Physical Chemistry. London (1910), 163 and 295.

Since the affinity constants of benzoic acid and the methyl ether of salicylic acid lie so close together, and we are at this time most concerned with these two acids, we have redetermined their constants and find that there is no question concerning their relative values. The results are as follows:

The specific conductivity of the water was $1.19.10^{-6}$ at 25°.

TABLE I.—*Benzoic acid.* $\propto \infty = 387$.

$\phi/1000.$	Λ	$100 \propto$	$K = 100\,k$
64	23.48	6.07	0.0061
128	32.93	8.51	0.0062
256	45.89	11.86	0.0062
512	63.09	16.31	0.0062
1,024	83.80	21.66	0.0058
	$K = 0.0061$		

This value agrees with that found by Jones and others [6] when their figures are recalculated in terms of the Kohlrausch units.

[6] *Pub. Carnegie Inst. Wash.* (1912), **170**, 116.

TABLE II.—*Methyl ether of salicylic acid.* $\propto \infty = 387$.

$\phi/1000.$	$\Lambda.$	$100 \propto.$	$K = 100\,k.$
32	18.35	4.74	0.0073
64	26.30	6.79	0.0077
128	36.81	9.51	0.0078
256	50.77	13.12	0.0077
512	69.46	17.95	0.0078
1,024	95.00	24.55	0.0078
	$K = 0.0077$		

This value agrees with that found by Ostwald [7] when his figures are calculated with the Kohlrausch units. If the above values are correctly given, it is evident that the affinity constants of acids are not necessarily measures of the rates of saponification of similar esters of the acids. At the present time sufficient data are not available to explain these anomalies.

Our method of approaching this problem has included a study of the hydroxyl group of phenol and its conversion in part and almost wholly into its sodium salt, a study of benzoic acid and of benzyl derivatives in which the $>C=O$ has been replaced by $>CH_2$, and finally of various ortho combinations of these groups, as found in *o*-cresol, *o*-hydroxybenzyl alcohol, *o*-hydroxybenzoic acid, its sodium salts, methyl ether, and the methyl ester of this ether.

PHENOL. FIG. 1

The absorption spectrum of phenol has been investigated by Hartley and Huntington;[8] Hartley, Dobie and Lauder;[9] and by Baly and Ewbank.[10] The last authors observed a shift in the absorption band in the presence of 4 equivalents of alkali, a condition which Baly and Desh [11] found in other compounds to be indicative of enol-keto tautomerism.

We have photographed this compound in neutral and acid alcohol solution and in the presence of 0.1, 1, 5, and 500 equivalents of sodium ethoxide, and have found that with the increase in the concentration of the sodium salt of phenol and corresponding decrease of free phenol, the absorption band becomes more

[7] *Zeitschr. f. physik. Chem.* (1889), **3**, 266.
[8] *Phil. Trans. Roy. Soc. London* (1879), **170**, 270.
[9] *Journ. Chem. Soc. London* (1902), **81**, 929.
[10] *Ibid.* (1905), **87**, 1347.
[11] *Ibid.* (1904), **85**, 1029; (1905), **87**, 766.

*Oscillation frequency* $(\frac{1}{\lambda})$.
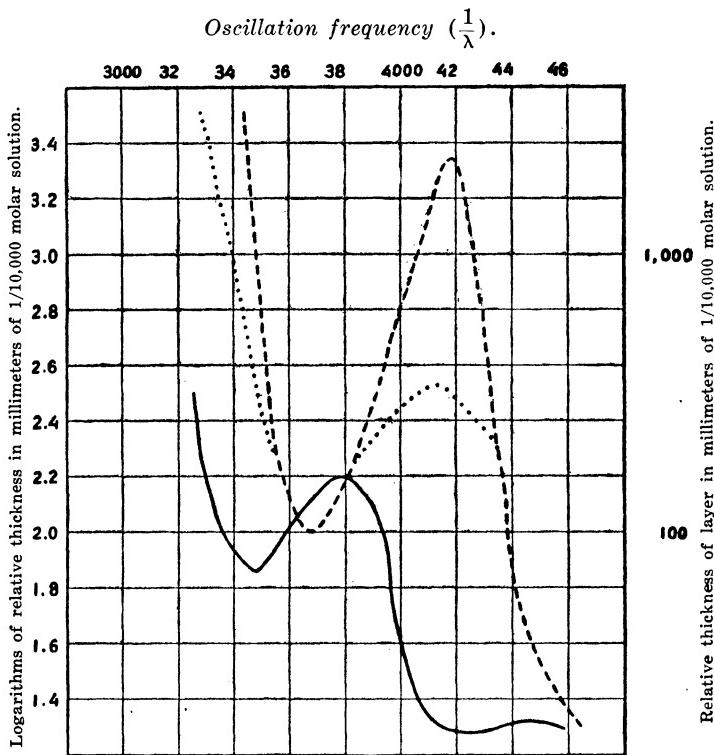
FIG. 1.—Dash curve = phenol.
  Dot curve = phenol with 1/10 equivalent of sodium ethoxide.
  Full curve = phenol with 5 equivalents of sodium ethoxide.

shallow, is shifted slightly toward the red, and gives every indication of disappearing entirely were all of the phenol in the form of the sodium salt.

The relative proportion of the phenol and sodium phenolate in water solution is obtained from the equation[12] $\frac{ne}{d} = 0.85 \times 10^{-4}$ in which n, e, and d are the concentration of the free base, phenol, and sodium salt, respectively. With 5 equivalents of alkali, approximately 98 per cent of the phenol is in the form of the sodium salt. We have not determined this hydrolysis constant in alcohol, but do not believe it to be very different. Under these conditions, the band characteristic of enol-keto tautomerism has diminished to a fraction of its original persistence, and a shallow band in the benzene region of the spectrum has made its appearance. The latter band also makes its

[12] Walker, Introduction to Physical Chemistry. London (1910), 336.

appearance in the presence of 1 equivalent of alkali. It is evident that the intramolecular vibrations of sodium phenolate more nearly approach those of the benzene ring. In fig. 1 the curve with 0.1 equivalent of alkali is plotted from dilution log. 3.5 to log. 2.3 which is the range obtained with 0.01 molar concentration. It is obvious that a dilution of this solution will change the value of d, so that this curve could not be farther continued with accuracy by this method.

The curve obtained with 1 equivalent of alkali is not plotted in fig. 1 since it falls between the curves of 0.1 and 5 equivalents. Similarly, that with 500 equivalents is omitted since it lies near that with 5 equivalents, but shows a further decrease in persistence of the band. The curve obtained in alcohol saturated with hydrogen chloride follows the curve of neutral phenol, except that the persistence of the transmission band at $1/\lambda=4180$ is reduced from log. 3.34 to log. 2.82. It is thus seen that acids and alkalies have a somewhat similar effect in reducing the persistence of the absorption band of phenol, which is to be interpreted as producing a more stable molecule.

To test the validity of this assumption, we have exposed to the sunlight tubes of phenol and phenol dissolved in a large excess of a concentrated solution of sodium hydroxide, and find that the former colors in a few hours while the latter fails to show any coloration after weeks of exposure. Sodium phenolate in solution is colored rapidly, but, in the presence of an enormous excess of alkali, the hydrolysis and also the ionization are at a minimum, and we probably have the stable form C_6H_5ONa. If it be granted that the oxidation of phenol is capable of explanation by reason of the transformation

$$HO \cdot C_6H_4 \cdot H \leftrightarrows O : C_6H_4 : H_2$$
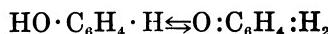
the two hydrogen atoms being oxidized with the formation of quinone, then it is readily seen that sodium phenolate will resist this transformation since the sodium atom has greater affinity for the oxygen than for the carbon.

O-CRESOL.   FIG. 2

The absorption spectrum of o-cresol has been investigated by Hartley [13] and by Baly and Ewbank. The latter authors observed the shift in the absorption band toward the red, which takes place in the presence of alkalies.

[13] *Journ. Chem. Soc. London* (1888), **53**, 641.

Oscillation frequency $(\frac{1}{\lambda})$.
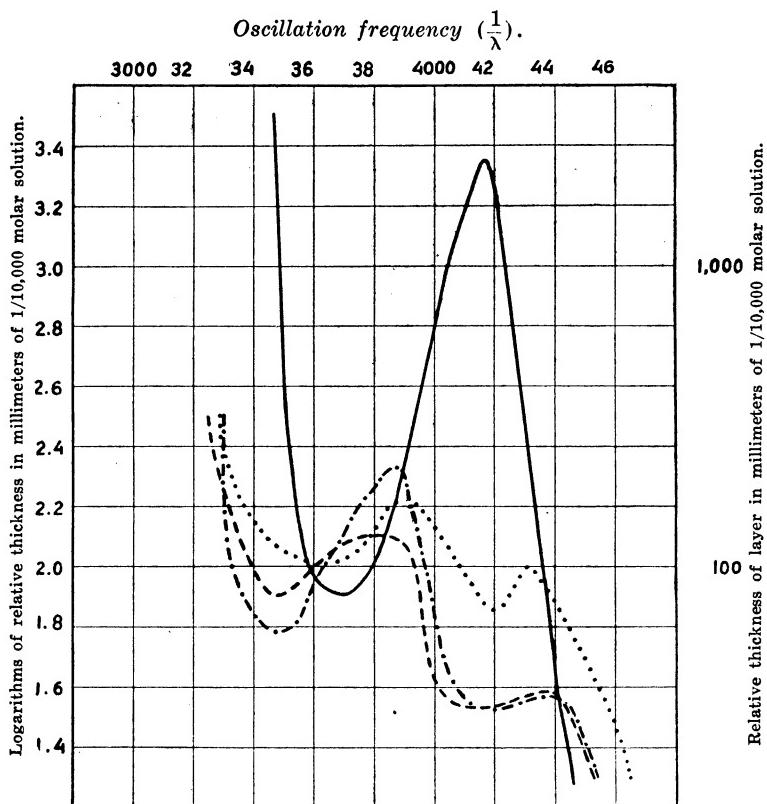
FIG. 2.—Full curve = *o*-cresol in alcohol.
    Dot curve = *o*-cresol with 1 equivalent of sodium ethoxide.
    Dash curve = *o*-cresol with 5 equivalents of sodium ethoxide.
    Dash and dot curve = *o*-cresol in aqueous solution with 5
        equivalents of sodium hydroxide.

The curves for *o*-cresol in alcohol and in the presence of alkali as shown by Hantzsch [14] cannot be correctly attributed to this compound. It is probable that acetoacetic ether was photographed instead of *o*-cresol, since the curves correspond with his data for the former compound. We have photographed *o*-cresol in alcohol solution and in the presence of 1 and 5 equivalents of sodium ethoxide, and in water solution in the presence of 5 equivalents of alkali. It is to be noted that an absorption band in the benzene region makes its appearance in the presence of alkali, a fact not noted by previous investigators. This band corresponds to that observed with phenol in the presence of alkalies, but appears at slightly greater concentrations.

[14] *Ber. d. deutschen chem. Ges.* (1910), **43**, 3071.

The persistence of the band heading at $1/\lambda=3480$ is much greater in alkaline aqueous solutions than in the corresponding alcohol solutions, a condition which points to the conclusion that the hydrolysis of the sodium salt is greater in aqueous than in alcoholic solutions.

O-HYDROXYBENZYL ALCOHOL.   FIG. 3

This compound was photographed in neutral alcohol solution and also in the presence of 5 equivalents of alkali.   See dot and dash curve and dot curve, fig. 3.   The conditions existing in phenol and *o*-cresol are also found in this compound.   The portion of the curve for 5 equivalents of alkali lying below log. 1.7 was obtained by photographing a 1/1000 molar solution.   Since this concentration was obtained by diluting a 1/100 molar solution,

*Oscillation frequency* $(\frac{1}{\lambda})$.
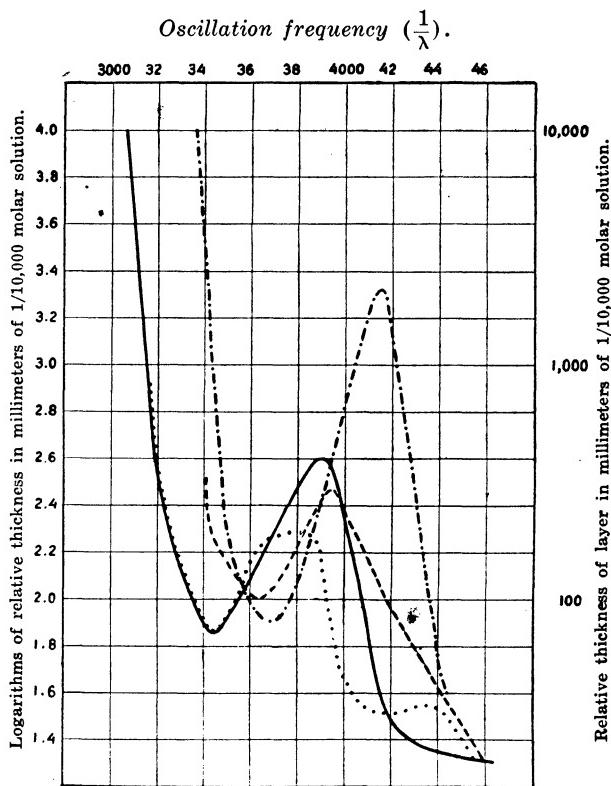
Fig. 3.—Dot and dash curve = *o*-hydroxybenxyl alcohol.
Dot curve = *o*-hydroxybenxyl alcohol with 5 equivalents of sodium ethoxide.
Full curve = methyl ether of salicylic acid and methyl ether of methyl salicylate.
Dash curve = methyl ether of salicylic acid with 5 equivalents of sodium methoxide.

it is clear that the degree of hydrolysis must be different. The two portions of the curve do not quite join, but the variation is so slight that it is not shown in the chart.

METHYL ETHER OF SALICYLIC ACID, AND THE METHYL ETHER OF METHYL SALICYLATE.   FIG. 3

The methyl ether of salicylic acid may be obtained easily and with a good yield by the following method. One hundred grams of salicylic acid and 70 grams of sodium hydroxide are dissolved in 300 cubic centimeters of water. This concentration of alkali converts about 97 per cent of the acid into the di-sodium salt. One hundred grams of methyl sulphate are added in small portions with constant shaking, keeping the temperature below 40°. When the methyl sulphate has disappeared, the solution is strongly acidified with hydrochloric acid and extracted with ether. The ether layer is separated, washed with water, and the ether removed by evaporation. The residue is heated for one hour on the water bath with an excess of lime water and filtered. The insoluble residue of calcium salicylate is repeatedly extracted with boiling water, and the combined filtrates acidified with hydrochloric acid. The methyl ether of salicylic acid is deposited upon cooling in large monoclinic plates. It should be recrystallized from water until ferric chloride shows no trace of salicylic acid. Its methyl ester is easily obtained with methyl alcohol and hydrogen chloride, and boils at 245-246°. This boiling point agrees with that found by Schreiner [15] and not with the lower value given by Fölsing.[16] The ester-ether was saponified, and the resulting acid identified as the methyl ether of salicylic acid. The absorption spectra of these two compounds in neutral alcohol solutions are identical. We have photographed them in the presence of 1 and 5 equivalents of sodium ethoxide. Under these conditions the absorption band heading $1/\lambda=3440$ in the methyl ether of salicylic acid is shifted toward the shorter wave lengths to $1/\lambda=3640$, both concentrations of alkali giving practically identical results. The persistence of this band is, at the same time, reduced, and the incipient band in the benzene region of the spectrum is lost. It is to be noted that, while alkali causes a shift toward the red in the compounds previously discussed, the shift in this instance is in the opposite direction. The former shift is characteristic of enol-keto tautomerism, and is not shown when the labile hydrogen atom is replaced by an alkyl group,

[15] *Ann. Chem. Pharm.* (1879), **197**, 1.
[16] *Ber. d. deutschen chem. Ges.* (1884), **17**, 486.

while the latter may be an ionization phenomenon. **Baly and Schaefer** [17] have pointed out from a study of cinnamylideneacetic, cinnamylidenemalonic, and other acids that the addition of alkali decreases, while the addition of acids increases, the free affinity of the carbonyl group, and state that the natural deduction from this is that the more the substance is ionized the less the free affinity possessed by the carbonyl group.

The amount of free affinity of the carbonyl group is greatest when the acid is not ionized and least in the easily ionized sodium salt.

The absorption curve of the methyl ether of methyl salicylate is neither shifted nor altered in any way in the presence of alkali. This behavior is to be expected from a nonionizable compound of this type.

It is interesting to note that the absorption bands heading at $1/\lambda = 3440$ of phenol, *o*-cresol, and of *o*-hydroxybenzyl alcohol, all in presence of 5 equivalents of alkali, almost coincide with that of the methyl ether of salicylic acid in neutral solution and of the methyl ether of methyl salicylate, and further that these 5 curves all show an incipient band in the benzene region. It is evident that under these conditions the internal molecular vibrations of these compounds are remarkably similar. In phenol, *o*-cresol, and *o*-hydroxybenzyl alcohol, the enol-keto tautomerism exists without the modifying influence of the carbonyl group, and the absorption curves of these three compounds and of their methyl ethers are almost identical. The replacement of the hydroxylic hydrogen atom of these compounds by sodium is thus seen to produce much the same effect as the adjacent carbonyl group produces in their ethers.

SALICYLIC ACID AND METHYL SALICYLATE.   FIG. 4

The absorption spectra of these compounds have been described by Hartley and Huntington [18] and Hartley,[19] but, for purposes of comparison with the other compounds described in this paper, we have photographed salicylic acid in alcohol, and its methyl ester [20] in neutral water and in alcohol solutions,

[17] *Journ. Chem. Soc. London* (1908), **93**, 1808.
[18] *Loc. cit.*
[19] *Journ. Chem. Soc. London* (1888), **53**, 641.
[20] Methyl salicylate was photographed in absolute alcohol solutions, and in aqueous solutions which contained sufficient alcohol to complete the solution. One-tenth molar solutions were made in 50 per cent alcohol, one-hundredth in 35 per cent alcohol, and one-thousand in 3.5 per cent alcohol.

Oscillation frequency $(\frac{1}{\lambda})$.
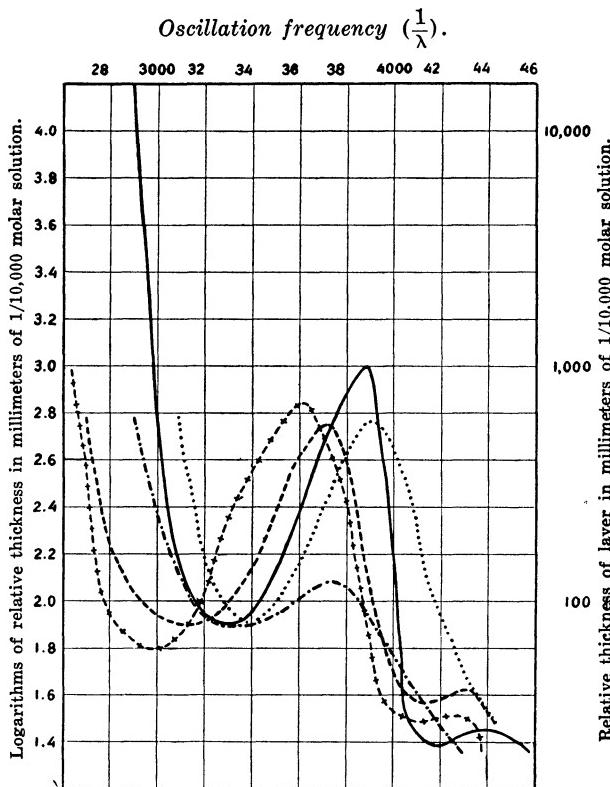
FIG. 4.—Full curve=salicylic acid and methyl sali-
cylate.
Dash curve=methyl salicylate with 1 equiv-
alent of sodium ethoxide.
Dot curve=salicylic acid with 5 equivalents
of sodium ethoxide.
Dot and dash curve=salicylic acid with 300
equivalents of sodium ethoxide.
Dash and cross curve=methyl salicylate with
500 equivalents of sodium ethoxide.

salicylic acid in alcohol in the presence of 5 and 300 equivalents
of sodium ethoxide, and methyl salicylate in alcohol in the
presence of 1/10, 1, 3, and 500 equivalents of sodium ethoxide
and in the presence of hydrogen chloride. We have observed
that the curves obtained with water and with alcohol as the
solvent are practically identical and in accord with data given
by Hartley.

The activity of the carbonyl group of salicylic acid is reduced
in the easily ionized sodium salt and also by the fixation of the
labile hydrogen atom by methyl. This is shown in the charts
of the absorption spectra both by a reduction in the persistence

of the absorption band of salicylic acid at $1/\lambda=3300$ and by a shift of this band to $1/\lambda=3400$, a position which corresponds to the same band shown by salicylic acid in the presence of 5 equivalents of sodium ethoxide. In the latter case the salicylic acid is almost entirely in the form of the mono-sodium salt (the actual amount of the salicylic acid in the form of the di-sodium salt is about 11 per cent of the whole), and the shift to the shorter wave lengths may be due to the ionization phenomenon previously mentioned. With 300 equivalents of alkali, the salicylic acid in one-thousandth molar solution is approximately 9.2 per cent in the form of the mono-sodium salt and 90.8 per cent in the form of the di-sodium salt for n $\times$ s/0.03=d where

    n=concentration of the free base,
    s=concentration of the mono-sodium salt,
    d=concentration of the di-sodium salt.

These values are computed for aqueous solutions since the hydrolysis constant in alcohol is not available. We believe the error thus introduced has no bearing on the general considerations.[21]

The absorption curve under these conditions is, therefore, that of di-sodium salicylate. The absorption band is much broadened; and the shift toward the shorter wave lengths, found in the presence of 5 equivalents of alkali, is more than counterbalanced by the shift toward the red which is characteristic of the enol-keto tautomerism. Since this absorption band has almost entirely disappeared, it is evident that the free affinity of the carbonyl group is approaching a minimum.

The curve for methyl salicylate in the presence of a small quantity of alkali, 1 equivalent, shows a shift toward the red and a decrease in the persistence of the large absorption band. In the presence of greater excess of alkali, the shift toward the red is increased, while no further reduction in the persistence is to be noted. The presence of acid causes no appreciable change in the absorption spectrum of methyl salicylate. Since the ionization constant of this compound [22] is very small; namely, 1.2×10^{-11}, it appears probable that no measurable effect is to be expected. All of the curves which have any significance are plotted in fig. 4.

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[21] In one-thousandth molar alcohol solutions the addition of 10 per cent of water was necessary to keep the salts in solution.

[22] *This Journal*, Sec. A (1913), **8**, 1.

Oscillation frequency $(\frac{1}{\lambda})$.
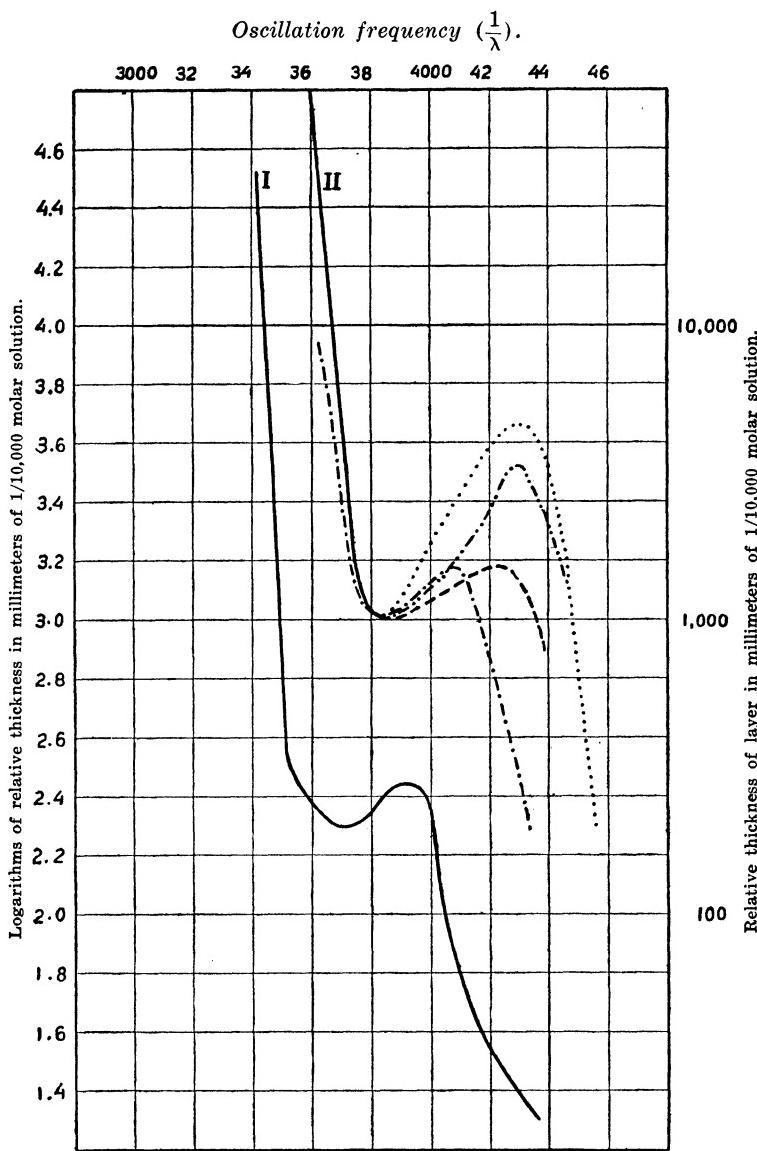
FIG. 5.—Curve I=methyl benzoate.
Curve II and dot curve=benzyl alcohol.
Curve II and dash-two-dot curve=benzyl acetate.
Curve II and dash curve=benzyl methyl ether.
Dash-dot curve=benzyl chloride.

BENZYL ALCOHOL, BENZYL ACETATE, BENZYL METHYL ETHER, BENZYL CHLORIDE, AND METHYL BENZOATE.   FIG. 5

The absorption spectra of benzyl alcohol and benzyl ethyl ether have been studied by Baly and Collie,[23] and since it did not seem probable that the absorption band at $1/\lambda=3600$ was correctly ascribed to this type of compounds by these authors and also for the reasons given above, we have included a study of benzyl alcohol and 4 closely related compounds in this investigation. Benzyl alcohol, acetate, methyl ether, and chloride were dissolved in pure ethyl ether and shaken repeatedly with dilute aqueous alkali, and then with water until neutral.   The ether layer was dried with anhydrous copper sulphate, the ether evaporated, and the residue fractioned several times under reduced pressure. This procedure was found necessary to obtain pure compounds. The substances thus prepared show only one absorption band which lies in the benzene region of the spectrum and heads at $1/\lambda=3850$ in each case.   The persistence of this band decreases in these compounds in the order in which they are mentioned from the maximum shown by benzyl alcohol.   From log. 3.0 to 4.8, and $1/\lambda=3600$ to 3850, the curves of the first three compounds are identical while that of benzyl chloride apparently shows slightly greater general absorption.   The divergence in the curve of the latter may be due to traces of impurities.   No indication of an absorption band in this region of the spectrum is shown by any of these compounds.   There is no doubt that their true absorption spectra bear little resemblance to the descriptions of Baly and Collie.   Absorption bands outside of the benzene region of the spectrum are not to be expected in compounds of this type.

The absorption curve of methyl benzoate is very similar to those of the benzyl derivatives, but appears at greater dilution, and the absorption band heads nearer the visible region of the spectrum; namely at $1/\lambda=3700$.   The absorption spectrum of the free acid has been described by Hartley and Huntington,[24] and it shows no noteworthy differences from that of methyl benzoate.[25]

[23] *Journ. Chem. Soc. London* (1905), **87**, 1343.

[24] *Loc. cit.*

[25] Baly and Collie (*loc. cit.*) state: "The spectrum of benzoic acid has been observed by Hartley and Huntington, and only shows general absorption rather strongly.   This is only to be expected from the presence of the ketonic oxygen in the β-position," a statement which does not seem to be strictly in accord with the facts.

ILLUSTRATIONS

THE ABSORPTION SPECTRA OF PHENOQUINONE, 2,5-DIANI-LINOQUINONE, 2,5-DIANILINOQUINONEANIL, AND 2,5-DIANILINOQUINONEDIANIL (AZOPHENINE)

By D. S. Pratt and H. D. Gibbs [1]

(*From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.*)

Two text figures

In the study of the compounds which cause the red color of phenol [2] it was pointed out that the coloration is due to the oxidation of phenol to quinone with the subsequent condensation to phenoquinone, although physico-chemical methods would be necessary to prove the presence of the latter compound. The most satisfactory method appeared to be based upon the absorption spectra of the compounds in question.

Phenoquinone, crystallized from ligroine, was dissolved in absolute alcohol, and the absorption spectrum photographed in the manner described in our previous work.[3] The absorption curves, plotted with logarithms of the dilutions and oscillation frequencies, are shown in fig. 1, and the curves of quinone and phenol in alcohol are included for purposes of comparison.

In alcohol, the color band shows in one-tenth molar solution and closely resembles that of quinone. Dilutions of this solution to hundredth and thousandth molar concentrations give curves that are not continuations of the tenth molar and of each other. This discontinuity upon dilution is not shown by quinone and phenol, and since these compounds follow Beer's law it is evident that dilutions of phenoquinone solutions do not give the expected concentrations of phenoquinone. This is due to dissociation which may be expressed by the equilibrium equation:

$$C_6H_4O_2 + 2C_6H_5OH \rightleftarrows C_6H_4O_2 \cdot 2C_6H_5OH.$$
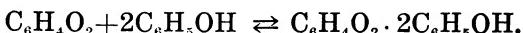
In order to test the validity of this assumption, we have dissolved in alcohol quantities of quinone and phenol calculated for tenth molar solution of phenoquinone and find that the absorption curve of this solution coincides with that obtained by dis-

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[1] Associate professor of chemistry, University of the Philippines.
[2] Gibbs, *This Journal, Sec. A* (1908), **3**, 364.
[3] *This Journal, Sec. A* (1912), **7**, 371; (1913), **8**, 33.

solving phenoquinone crystals in alcohol. These two solutions are in fact identical. Since the curve obtained with tenth molar solutions so closely resembles the quinone curve, and for other reasons, it is evident that the actual amount of phenoquinone in solution at this concentration is very small.

If the above equilibrium reaction is correctly represented, an increase in the concentration of phenol should result in a greater concentration of phenoquinone, and in phenol as a solvent the dissociation of phenoquinone should be at a minimum. The curves obtained with an excess of 8 equivalents of phenol and in pure phenol show this assumption to be justified. The most striking characteristic of these curves is the change from a definite absorption band shown in quinone to a mere step off in phenoquinone in phenol and also the greatly reduced concentration at which the incipient band appears. From this it is evident that the red color of phenoquinone is largely due to general absorption, and it is probable that the isorropesis present in phenoquinone is quite different from that in quinone. This difference, it seems to us, is due to a loss of the free affinities of the two carbonyl groups, and may be best expressed by the oxonium structure

$$H \diagdown \diagup OC_6H_5$$
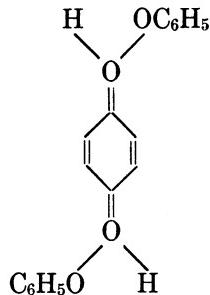
This representation accounts for the instability of the compound, the dissociation in solution, and the formation of its very unstable salts better than the formulas of Jackson and Oenslager [4] and of Willstätter and Piccard.[5]

The conditions existing in dianilinoquinone, dianilinoquinone-anil, and azophenine are quite different. In all of these compounds the quinone absorption band is well marked, and in

[4] *Ber. d. deutschen chem. Ges.* (1895), **28**, 1614; and *Am. Chem. Journ.* (1896), **18**, 1.

[5] *Ber. d. deutschen chem. Ges.* (1908), **41**, 1458.

azophenine the isorropesis occurring between the two unsatu-
rated nitrogen atoms in the para position produces the same
effect as the carbonyl groups.   Since the absorption bands are
well developed and in much the same positions when phenol is
employed as the solvent, it is evident that the absence of a well-
marked phenoquinone band in this portion of the spectrum is
not to be attributed to this solvent.

The dilution at which the band characteristic of the quinoid
structure makes its appearance is dependent upon the nature of
the adjacent groups, since this band is shown in tenth molar
solutions of quinone and in thousandth or ten-thousandth molar
solutions of the other compounds mentioned.   The argument
employed by Baly, Tuck, and Marsden [6] that the bands of the
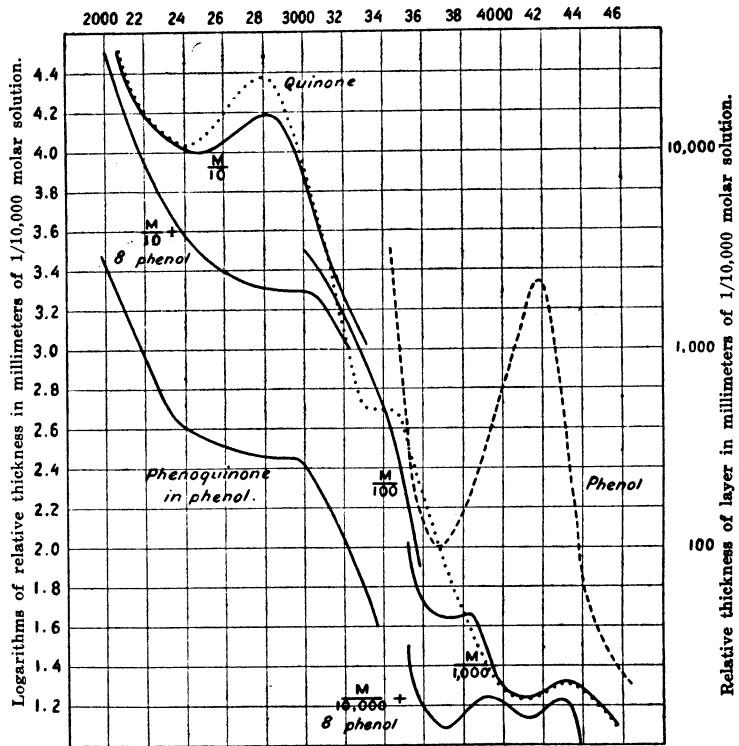

FIG. 1.—Full curves = phenoquinone.
      The upper in alcohol, the middle in alcohol with 8 equiv-
      alents of phenol, and the lower in pure phenol.
      Dot curve = quinone in alcohol.
      Dash curve = phenol in alcohol.

[6] *Journ. Chem. Soc. London* (1910), **97**, 588.

nitrophenols in presence of alkali are not quinone bands for the reason that they appear at greater dilutions than in quinone itself is thus seen to be without weight.

In order to prove that phenoquinone is produced in phenol by oxidation, we have exposed colorless phenol in open vessels to the action of sunlight until it developed a decided red color, after three or four days, and then photographed its absorption spectrum. The curve was found to coincide with that of phenoquinone dissolved in phenol. The proportion of phenoquinone formed by the action of sunlight and oxygen in a given time can be estimated by comparison with the curves shown in fig. 1.

Fig. 1. The curves of quinone, phenol, phenoquinone in alcohol, phenoquinone plus 8 equivalents of phenol in alcohol, and phenoquinone in pure phenol are shown. Our curve of quinone practically agrees with that given by Baly and Stewart,[7] except that the small band in the benzene region heading at $1/\lambda=4100$ is not shown in their charts. Hartley, Dobbie, and Lauder [8] show this band highly developed, but it is probable that the pure compound will show no band in this region of the spectrum. Since quinone is so readily reduced by alcohol in ultra-violet light, it is reasonable to attribute this incipient band to the presence of small quantities of quinol.

The curves of phenoquinone in alcohol in tenth, hundredth, and thousandth molar concentrations have been previously described. The absorption band at $1/\lambda=3700$ is due to phenol and that at $1/\lambda=4100$ to quinone. The curve of phenoquinone with 8 equivalents of phenol obtained with hundredth molar solution is not shown on the chart, since it is almost a straight line and lies very close to that of hundredth molar phenoquinone. The phenol band at $1/\lambda=3700$ shows in this solution at log. 1.1, since the phenol is present at one-thousandth molar concentration.

Fig. 2. Since dianilinoquinone is insoluble in alcohol and in the usual diactinic solvents, it is necessary to employ glacial acetic acid to cover approximately the full range of the absorption spectrum. In order to obtain comparisons of the color band of this compound with those of dianilinoquinoneanil and azophenine, we have also used solutions in aniline and in phenol. The curves are shown in fig. 2.

[7] *Ibid.* (1906), **89**, 507.
[8] *Rep. Brit. Assoc.* (1902), 99.
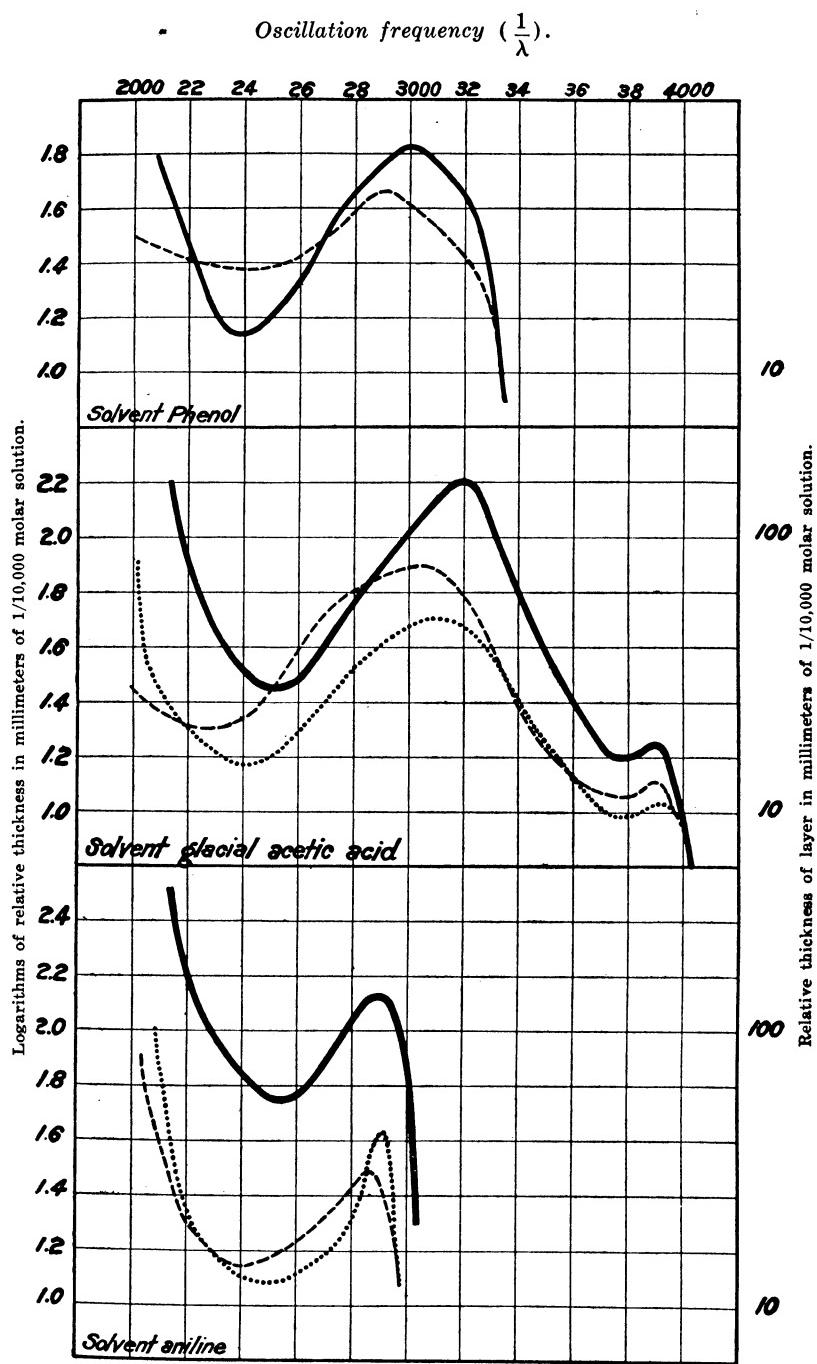
FIG. 2.—Full curve＝2,5-dianilinoquinone.
Dot curve＝2,5-dianilinoquinoneanil.
Dash curve＝azophenine.

It is to be noted that the curves for dianilinoquinone are similar within the limits of the solvent in each case. The greatest variation due to the solvent is found in azophenine. The color band in phenol and in glacial acetic acid is much extended toward the red, and the general absorption is greatly increased over the curve shown in aniline. This condition is probably due to the acid nature of the solvents, phenol and acetic acid. The color bands of these three compounds are well defined in each solvent, and clearly indicate quinoid structure, which accords with the formulas assigned to them.

ILLUSTRATIONS

PHILIPPINE FRUITS: THEIR COMPOSITION AND CHARACTERISTICS

By D. S. Pratt and J. I. del Rosario

(From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.)

Sixteen plates

INTRODUCTION

From the days of the earliest explorer, tropical fruits have been held in high esteem. The reports of those who had eaten these food products were often grossly exaggerated, but they served to stimulate the spread and cultivation of many important varieties. Improvements in transportation and a growing demand have resulted in placing many tropical and semitropical fruits in northern markets. Other varieties are equally valuable, and doubtless in time will form the basis of an extensive export trade when methods of preserving and canning are more perfectly understood.

Practically no systematic work has been carried out in studying the chemical composition of tropical fruits, and few data are available concerning any except the citrus fruits, the banana, and the pineapple. It is hoped that complete analyses with descriptive notes and illustrations of our principal fruits may serve a useful purpose in calling attention to the economic possibilities involved, and aid future work in this important commercial field.

The term "fruit" as popularly understood includes the edible portion of many shrubs and trees both wild and cultivated. In a narrower sense the berries and vegetables are excluded, although the line of demarcation is not sharp and is often dependent upon the condition of the food product in question. Thus many fruits in a partially matured state are cooked and served as vegetables.

The chief characteristics of fruits are their color, texture, odor, flavor, and nutritive properties. All varieties contain a high percentage of water, holding in solution sugars and acids, together with small amounts of mineral matter. The individual odor and taste are dependent upon traces of compound ethers and esters present in amounts that preclude identification in most cases, but which are very important in making the fruit

palatable. The solid portion comprises the usual cellulose plant structure. Fruits also contain a group of substances called pectin and pectose, the exact nature of which has not been definitely determined. The latter gives to unripe fruits their characteristic hardness and indigestibility. During the course of ripening, insoluble pectose is gradually transformed into soluble pectin, a carbohydrate related to starch and sugar. Pectin gelatinizes upon boiling, and fruit rich in this peculiar class of compounds may be utilized in making jelly, as it is upon them that the setting power of the juice depends.

The nutritive value of fruits lies chiefly in the sugars present, although the acids and salts exercise an important function in the digestive processes. The high water content, with correspondingly low percentages of proteins, carbohydrates, and fats, indicates a much less important place for fruits in a dietary than they actually deserve. A relatively high amount of iron is present in almost all varieties and may thus be added to the diet without replacing staple articles of food. It must also be remembered that fruits supply bulk and exert a beneficial laxative tendency. These properties are all of value in opposing the conditions favorable to excessive intestinal putrefaction. In warm climates especially, sound ripe fruit should form a part of the daily food of the people.

METHODS OF ANALYSIS

The methods of analysis are of great importance in dealing with complex material such as fruits, and without information on the procedure followed the data obtained are often of little value. For the purposes of this investigation, in every case not specified, ripe fruits in sound condition were studied.

The edible and waste portions were carefully separated, and the former passed through a meat grinder until uniform representative samples could be obtained. The determination of total solids was carried out by drying, first on a steam bath, then to constant weight at 80°C.

Insoluble solids were determined by repeated extraction with warm water of 20-gram samples on a folded filter and drying the resulting solid at 80°C. The combined filtrates were titrated with tenth normal alkali using phenolphthalein as indicator, since this gives the most accurate total acidity. This value is expressed in terms of the acid actually present, and also as sulphuric acid for purposes of comparison. The fruit acids were

identified [1] in every case, although traces of other acids, present chiefly as salts, are probably also factors in the composition.

Sugars were determined both by copper reduction and by polariscopic readings before and after inversion. Sucrose was calculated by Clerget's formula. The percentage of total invert sugar after inversion divided by the percentage of acidity expressed in terms of sulphuric acid gives what may be called the sugar ratio. This is a measure of the apparent degree of sweetness, and is useful in comparing different fruits. Ten-gram samples were used in the Gunning method for nitrogen. The results are expressed as protein (nitrogen × 6.25). Starch was determined by acid inversion when present in appreciable amounts.

It is a common practice throughout the Islands for the native fruit growers to send their products to market in an immature condition. This is apparently done to avoid theft, and has resulted in creating a demand for green fruits that are far inferior in size and flavor to what could be expected under normal conditions.

The many types of citrus fruits and bananas have been reserved for a future publication, as the collection at present being made by the Bureau of Agriculture is incomplete and specimens are not available.

The botanical descriptions were made by Mr. E. D. Merrill of the Bureau of Science.

The following abbreviations for the various native languages are used throughout the paper:

> Sp. Fil. = Spanish Filipino.
> T.   = Tagalog.
> V.   = Visayan.
> Il.   = Ilocano.
> Pamp. = Pampangan.

THE MANGO

MANGIFERA INDICA L. Plate I; Plate II, fig. 1. MANGO; MÁNGA T., V., Il.; PAHO, V.

A large tree with glabrous, oblong or lanceolate leaves and terminal panicles of small yellow flowers. Fruit large, yellow, fleshy, ellipsoid to oblong-ovoid, equally rounded or narrowed and somewhat pointed at one end, up to 18 centimeters long, the

[1] *Cir. U. S. Dept. Agr., Bur. Chem.* (1911), **76**; (1911), **87**; (1911), **88**.

pulp abundant, closely surrounding the large compressed seed which is fibrous, especially along the edges.   Tropical Asia.

The mango is one of the most important and delicious fruits of the world, and takes the place in tropical countries of the peach.   It is consumed in immense quantities, and forms a staple article of diet during its rather long season.   The tree is held sacred in India, and references to it are woven through the native folklore and poems.   In the Indian story of Súrya Bai[2] the daughter of the sun is represented as persecuted by a sorceress, to escape from whom she became a golden lotus.   The king fell in love with the flower, which was then burnt by the sorceress.   From its ashes grew a mango tree, and the king fell in love first with its flower, and then with its fruit.   When ripe the fruit fell to the ground, and from it emerged the daughter of the sun who was recognized by the prince as his lost wife.

The seeds contain about 10 per cent tannin, and are used with beneficial effect in certain cases of dysentery.   The bark and leaves contain a yellow dye of slight importance.

Mangos are prepared for consumption in a variety of different forms.   The green, strongly acid fruit is boiled with sugar or pickled, is used in curries, and to flavor many fish products.   The largest demand is for the ripe fruit, and good specimens often sell for 2 pesos[3] a dozen in the Manila market when bought in small quantities.   They are eaten by everyone, and are the best fruit produced in the Islands.   The pulp of a fully ripened mango is rich golden orange, very juicy, and recalls slightly the taste of a peach.   It is excellent in salad or ice cream, and should find an unlimited market if properly canned.   Three types enter the markets, differing slightly in size, shape, and flavor.   The most important and finest is the carabao (Plate I, fig. 1). ,The pico (Plate I, fig. 2) is slightly smaller and lacks some of the spicy flavor found in the carabao.   The pahutan (Plate II, fig. 1) is decidedly smaller and slightly sweeter, but its low proportion of edible pulp makes it less valuable for commercial purposes.   Other varieties are found in the different islands, but many have a disagreeable taste resembling turpentine and are unimportant.   Among these may be mentioned the large mango known as "juani" of Jolo and Mindanao.

The mango season begins about the first of April, and extends through July, although the Filipinos often force the fruit by building fires under the trees or chopping the bark.   A few

[2] Cox, Mythology of the Arian Nations.
[3] One peso Philippine currency equals 50 cents United States currency.

inferior mangos are found in the markets of some localities during the entire year.

CHICO

ACHRAS SAPOTA L. Plate II, fig. 2. CHICO; SAPODILLA PLUM; ZAPOTE, BULLY-TREE; NASEBERRY.

A small tree with milky sap, the leaves thick, shining, entire. Flowers small, fascicled, axillary. Fruit globose to ovoid, brown, usually 4 to 5 centimeters in diameter, the pulp brownish, granular, containing from 1 to 5 large, hard, shining black seeds. Native of tropical America.

The chico is one of the best fruits grown in the Islands. Firminger states that

> A more luscious, cool and agreeable fruit is not to be met with perhaps in any country in the world.

It is common in many parts of the Tropics, especially the West Indies, Central America, Mexico, and India, and is highly esteemed wherever known. The pulp is firm, abundant, and has a sweet taste not unlike the flavor of maple. The unripe fruit is high in tannin and gum, but these disappear during ripening, and leave a juicy pulp that is excellent.

The gum is distributed throughout the tree, and is a valuable commercial product. It is collected in many parts of Mexico and Central America under the name "gum-chicle," but especially in Yucatan where an extensive trade has been built up. The milky juice is gathered from incisions made in the bark, considerable skill being necessary to avoid harming the tree. Tapping should occur only once in three years. The juice is boiled to proper consistence, and molded in bricks for export. Overheating causes the gum to turn reddish, and reduces its selling value. The first quality chicle is firm, almost white, aromatic, and nearly tasteless. It is the basis of chewing gum and has a ready market. There seems to be no reason why it could not be collected here, and with cultivation form a considerable source of profit, although at present the trees are too scattered to compete with Yucatan. Good quality chicle sells for 35 to 45 cents a pound in the New York market.

JAK

ARTOCARPUS INTEGRIFOLIA L. f. Plate III, fig. 1. JAK; LANCA, NÁNCA, NÁÑGCA, T.; ANAÑGCA, Il.

A small or medium-sized spreading tree with abundant milky juice. Leaves elliptic, obtuse, entire. Fruits solitary, very large, up to 50 centimeters long, borne on the trunk and larger

branches, oblong, compound, green, muricate, containing many rather large seeds, each surrounded by the edible pulp. Tropical Asia.

The name "jak" was given by the early Portuguese from the Malay *tsjka*. It is the largest of Philippine fruits, and attains a remarkable size. Specimens have been reported from Ceylon and India that weighed over 50 kilograms, although the usual size found in the markets is nearer 20. The fruit, or more properly infructescence, is of irregular shape, with the green surface broken up into roughly hexagonal knobs. The outer skin exudes a sticky, milky juice when cut that contains a small amount of caoutchouc. The interior of the fruit is yellow to cream color, and is divided into segments each containing a seed. The pulp has a strong odor said to be due to ethyl butyrate, and a rather sickening sweet taste that seldom finds favor with Europeans. The fruit is popular with the Filipinos, and is eaten both cooked and as gathered. It is roasted or baked, and also preserved with sugar as a sweetmeat.

Throughout the western coast of India and in lower Burma, jak is the chief fruit during the hot weather. When the syncarps mature, the fleshy arils are readily separated. They may be eaten at once, fermented to give an alcoholic beverage, or dried in the sun. This produces chips that are easily preserved until needed, and may then be boiled with salt to furnish a satisfactory food.

The seeds contain a large amount of starch, and are eaten after roasting, when they resemble Italian chestnuts. Flour may be made from the mature seeds, a single fruit of average size giving about 1 kilogram of chips and half as much flour. The entire tree, but especially the wood, contains a yellow dye of slight importance in India and Burma.

BREADFRUIT

ARTOCARPUS COMMUNIS Forst. (*A. rima* Blanco.) BREADFRUIT; RIMA, RIMO, T.; PAKÁK, Il.

A medium-sized tree with large, pinnately incised leaves. Fruits globose, green, muricate, compound, 10 to 12 centimeters in diameter, seedless, the pulp rather stringy, soft. Polynesia.

The ripe pistillate inflorescence forms one of the chief native foods in the South Sea Islands where it reaches a perfection and excellence never attained in the Philippines. The structure of the fruit resembles the jak, and the edible flakes are similarly

used.   It is of some importance in Ceylon and Burma where it is cultivated.   Firminger records that the sliced and roasted breadfruit is "hardly distinguishable from an excellent butter pudding."

ARTOCARPUS COMMUNIS Forst. (*A. camansi* Blanco.)   Plate III, fig. 2.

Very similar to the preceding variety, differing chiefly in the fruits bearing numerous rather large seeds.   Polynesia. Unimportant.

<div align="center">CASOY</div>

ANACARDIUM OCCIDENTALE L.   Plate IV, fig. 1. CASHEW, CAJU; CA-SÚY; CASÓY, T.; BOLLÓGO, Il.

A small tree with simple leaves and terminal panicles of small flowers.   Fruits consisting of two parts, the much enlarged, soft, yellowish, obovoid edible pedicel which is usually about 5 centimeters long, bearing at its apex the kidney-shaped seeds containing a caustic juice, edible only after being cooked. Tropical America.

The unripe fruit is very astringent, but when mature it becomes juicy and sweet, with the property of quenching thirst that adds to its value.   The outer skin is slightly irritant when applied to the skin, and has a smooth oily surface.   The pulp is fermented in Brazil and made into an alcoholic beverage that is said to resemble Madeira and have beneficial properties in stimulating the liver.   A similar intoxicating drink called "kaju" is consumed by the natives in eastern tropical Africa, and the juice is a source of very weak alcohol in Bombay.

The seed is enclosed in a grayish brown cellular shell that contains an essential oil possessing a blistering action due to the presence of cardol and anacardic acid.   This oil has a slight value as a preventive against white ants in wood, books, etc., and is used in the Andamans to color and preserve fish nets.

The kernel is edible after roasting, and so prepared is one of the best nuts available.   Cashew nuts are an article of commerce, and are in demand for confectionery and flavoring purposes. A fixed oil may be expressed from the nut that is very nutritious and the equal of almond oil in every respect.   The casoy beans sell for 5 centavos a hundred in the provinces, and trees bear after four years.   The nuts are used at present to a very slight extent, although there are possibilities of profit from this source.

TABLE I.—*Analysis of casoy nuts.*

Average weight of nut kernel, 2 grams.

	Per cent.
Oil	57.38
Protein	18.00
Starch	5.28
Fiber	0.91
Ash	2.42
Moisture	16.01

Constants of casoy oil.

Refractive index	1.4664 at 29°.5.
Saponification number	190.0
Specific gravity	0.9114 at 28°.8.
Iodine number (Hanus)	36.66

The oil is of a light yellow color, possesses a bland taste, and may be used for the same purposes as the best grade of olive oil. A yield of about 40 per cent may be obtained by pressing.

ANONA

ANONA MURICATA L. Plate IV, fig. 2. GUABANO; SOURSOP; GOYABÁNO, GUANABÁNO, Sp. Fil.; GUAYABANO, Il:

A small tree about 5 meters high, with oblong-ovate leaves 8–18 centimeters long. Fruit aggregate, fleshy, irregular, oblong-ovate to conical, greenish, covered with soft scattered spines, the flesh white, rather fibrous, subacid. Native of tropical America.

The ripe fruit possesses antiscorbutic properties, and a pleasant acid taste, although the pulp is rather stringy with black seeds scattered throughout. The juice bears a slight resemblance to pineapple in taste, and may be used as a refreshing beverage.

A fermented drink of agreeable taste not unlike cider is made from the juice of this and the other species of anona in the West Indies, where the fruits are plentiful. The fruit is one that possesses possibilities of value if preserved or canned, as it is excellent in salads and desserts and is available in sufficient quantity.

ANONA SQUAMOSA L. Plate V, fig. 1. CUSTARD APPLE; SWEET SOP; SUGAR APPLE; ATES, Sp. Fil.; ATIS, Il.

A small tree with simple, oblong-ovate leaves 6 to 12 centimeters long, pale beneath. Flowers 1 to 3, opposite the leaves, 2.5 to 3 centimeters long. Fruit soft, fleshy, glaucous, aggregate, irregularly heart-shaped, 7.5 to 10 centimeters long, tuberculate, the flesh sweet. Seeds numerous, dark brown. Native of tropical America. The ripe fruit easily separates into segments

that contain a white, creamy pulp of sweet taste.   The ates is of considerable importance, and is the most widely grown anona in the Philippines.   The preceding species is of slightly more commercial importance, as the proportion of edible pulp is greater and better suited for canning or preserving.

ANONA RETICULATA L. BULLOCK'S HEART; ANONAS, Sp. Fil.

A small tree with lanceolate, acuminate leaves 12 to 30 centimeters long, the flowers 1.5 to 3 centimeters long, leaf-opposed. Fruit 7.5 to 15 centimeters long, aggregate, fleshy, heartshaped; the surface nearly smooth, greenish yellow, more or less reticulate; the flesh soft, yellowish-white, sweet.   Native of tropical America.

This species is of only slight importance in the Islands, and seldom reaches the market, although in Jamaica and the other West Indian Islands the closely allied *Anona cherimolia* is held in high esteem.   There is no reason why anonas should not be grown more abundantly here, since the flavor is good and the fruit valuable.

CAMIAS

AVERRHOA BILIMBI L.   Plate V, fig. 2. CAMIAS, CALAMIAS, T.; PIAS, Il.

A small tree with pinnate, pubescent leaves, the leaflets up to 17 pairs, oblong, acuminate.   Flowers purplish, small, racemose, the racemes short, fascicled on the trunk and larger branches. Fruit green, cylindric, 5 to 7 centimeters long, round or nearly so in cross section, very acid.   Tropical America.

The small cucumber-like fruit is well known throughout the Philippines, and is eaten green, pickled, especially with fish, and preserved.   The strong acidity is due to oxalic acid, making the juice of use in removing ink stains or iron rust, and in polishing brass ware.   This and the closely related bilimbi are the only fruits of importance containing oxalic acid, emphasizing their position in the oxalis family.   The confusion in calling *A. bilimbi* the camias, and *A. carambola* the bilimbi is to be noted.

BILIMBI

AVERRHOA CARAMBOLA L.   Plate VI, fig. 1. BILIMBI, BILIMBÍN, BALIMBING, T.; GARANGÁN, V.; DALIGÁN, Il.

A small tree with pinnate glabrous leaves; the leaflets ovate, about 5 pairs; the small purplish flowers axillary.   Fruit green, acid, oblong-ovoid, 5 to 7 centimeters long, longitudinally 5-lobed, star-shaped in cross section.   Tropical America.

The general characteristics of this fruit are much like the preceding, and its uses are the same. The sour juice is useful as an antiscorbutic and as a cooling drink to allay fevers. Both form excellent preserves, with a pleasant refreshing taste.

PINEAPPLE

ANANAS SATIVA Lindl. PIÑA.

An erect perennial plant, the long spiny leaves forming a rosette, the fruit solitary, peduncled, erect, borne in the center of the rosette, fleshy, ovoid to cylindric, up to 40 centimeters long, more or less scaly, crowned by a tuft of leaves. Tropical America.

The fruit is so well known in every country that little need be said regarding it. The dietetic value is high, not only due to the available food material, but also to the presence of bromelin, a proteolytic enzyme closely related to trypsin. This ferment converts albuminous matter into peptones and proteoses, acting in acid, alkaline, or neutral media. The Philippine pineapples are of good size and flavor, although not equal to those from Hawaii. The industry of growing and canning pineapple is beginning to develop, and has great commercial possibilities. The fiber is used extensively in weaving the well-known piña cloth.

LIMONCITO

TRIPHASIA TRIFOLIATA DC.

A small spiny shrub with trifoliolate leaves and white flowers. Fruit globose, aromatic, red or purplish, about 1.5 centimeters in diameter, containing few seeds. Tropical Asia.

The limoncito was largely employed at one time for preserves, but its use has gradually declined as other and more suitable products became better known. It is eaten in India, and is very commonly used as an ingredient of Chinese preserved fruits.

POMELO

CITRUS DECUMANA Murr. Plate VI, fig. 2. POMELO, SHADDOCK, FORBID-DEN FRUIT; SUHA, LUCBAN, T.; SUÁ, Il.

A medium-sized, usually spiny tree, the leaves simple, the petiole foliaceous, often nearly as broad as the leaves. Flowers white, fragrant. Fruit large, globose, green or yellowish, 10 to 15 centimeters in diameter, the pericarp very thick, the pulp yellowish to pink, acid, usually containing numerous seeds in each segment. Tropical Asia.

A common product resembling grapefruit, but less succulent. The segments are generally separated or shredded for salads, and the fruit is preserved in sugar for jams, etc.

PAPAYA

CARICA PAPAYA L.   Plate VII, fig. 1.

Erect, normally unbranched plants, 10 meters high or less, the trunk soft, marked with large scars, the large palmately lobed leaves crowded at the apex of the stem.   Male flowers slender, in pendulous inflorescences.   Female flowers much larger, axillary, or on separate trees.   Fruit melon-like, globose to oblong, green or yellow, smooth, up to 40 centimeters in length, the pulp soft, yellow, the seeds very numerous, small, borne in 3 rows along the hollow interior.   Tropical America.

The green fruit is used for pickling or as a vegetable, and, when ripe, as a melon or in salads, desserts, etc.

The milky juice, especially of the green fruit, contains a valuable enzyme first separated by Peckholt.   It may be prepared for use by drying the crude juice in flat trays exposed to the heat of the sun, or a more active product made by precipitating with alcohol and drying over calcium chloride.   The dry residue is marketed under the name papoid, and the more active alcoholic precipitate as caricin, papain, or papayotin. The proteolytic action is similar to that of pepsin, but is greatest in alkaline solution, and is therefore valuable in stimulating intestinal digestion.

The leaves and green fruit have long been employed to render meat more tender.   The method followed is to allow the sliced fruit to remain on the meat some hours before cooking.   The leaves impart a characteristic flavor, probably due to the presence of the alkaloid carpaine.

The papaya varies in shape from the round female fruit to the long cylindrical hermaphrodite, both of which are practically the same chemically.   The male plant occasionally produces bisexual flowers, and small globose fruits that are much inferior in taste.

MELON

CUCUMIS MELO L.   Plate VII, fig. 2; Plate VIII, fig. 1. Melón, Sp. Fil.; Atimón, Catimón, V.

An annual, herbaceous, tendril-bearing vine, with small yellow flowers and subglobose to ellipsoid fruit 10 to 20 centimeters long, smooth or somewhat rough externally, uniform in color or slightly mottled.   Tropical Asia.

Two types of melon are found in the market, the smooth mottled one known as "melón" and the rough yellow surfaced "melón-español". The latter has a much better flavor, but is less used because of its higher cost. Neither form is equal to the melon of temperate climates.

WATERMELON

CITRULLUS VULGARIS Schrad. Plate VIII, fig. 2.

The watermelon is too well known to require description or comment. The Philippine product is small and of slightly inferior flavor, depending upon the season.

MABOLO

DIOSPYROS DISCOLOR Willd. Plate IX, fig. 1. MABOLO, AMÁGA, T. V.;
TÁLANG, T. Pamp.

A medium-sized tree with oblong coriaceous leaves, which are green above, paler and pubescent beneath. Flowers small, axillary. Fruit subglobose, up to 10 centimeters in diameter, red to yellow or brown externally, and velvety, the pulp rather firm with a strong odor. Seeds large, usually 5 or more in the center of each fruit. Indigenous.

The fruit has a peculiar fragrance resembling a perfume and mealy pulp not unlike some varieties of apple. The taste is sweet and appreciated by those who do not object to the odor. Of slight importance as a food.

DUHAT

EUGENIA JAMBOLANA Lam. Plate IX, fig. 2. LUMBOY, Sp.; DUHAT,
T. V. Pamp.

A medium-sized tree with elliptic, coriaceous, smooth leaves and small flowers in short panicles. Fruit ellipsoid or oblong, 2 to 2.5 centimeters long, the pulp dark purple surrounding a single oblong seed. Tropical Asia.

The duhat is eaten in large quantities by the Filipinos, especially by the children with whom it is very popular. A tincture made from the seed is employed to some extent as a cure for diabetes mellitus, but no important constituent that would justify its use has been isolated. The juice is a promising material from which to make wine, as the color and flavor are satisfactory and the fruit available in sufficient abundance. The fruit may be made into jelly equal in color and flavor to that of the guava.

TAMARIND

TAMARINDUS INDICA L. Plate XVI, fig. 2. TAMARINDO, Sp. Fil.; SAM-
PALOC, T. Pamp.; SALAMAGUI, Il.; SAMBAG, V.

A large tree with pinnate leaves, numerous small leaflets, and rather small yellowish flowers. Fruit a fleshy, cylindric,

olivaceous or brownish, indehiscent pod usually about 10 centimeters long and 2.5 centimeters in diameter, the few seeds imbedded in the firm pulp. Tropical Africa.

Tamarind is an important food product in many tropical countries, and is used in a great variety of ways. The young pods are cooked with fish and rice. The brown paste surrounding the seeds in the mature bean is removed from the pods and sold in balls weighing about 100 grams. These are used in similar preparations, and to form a refreshing laxative drink popularly supposed to benefit the liver, stomach, and blood. The pulp is also largely used to adulterate guava jelley, as it is much cheaper and supplies the requisite acidity. The substitution may easily be detected by the presence of tartaric acid in the product as this is absent in true guava jelly. The composition of the ripe tamarind pulp is very interesting, since it contains more acid and more sugar than any other natural food product. The large amount of acid so masks the 40 per cent of sugar present that the taste is decidedly sour. Large quantities of tamarind pulp are available in the northern provinces that might profitably be converted into an alcoholic beverage, and the seeds used as a source of oil. Tamarind oil was submitted to the Agriculture Horticultural Society of India in 1856, and a favorable report made at that time. The oil resembles linseed, but has greater siccative properties, and is suitable for varnish or paint. The seeds are also edible after soaking in water and boiling to remove the outer covering, when the resulting flour may be made into cakes and bread. The roasted seeds are superior to peanuts in flavor, and a valuable food. Indian tamarind pulp is preserved by heating in sugar sirup until saturated, and packing in earthenware pots glazed on the outside only. The jars are then filled with more sirup, and stored until the fruit becomes mellow, when it is shipped to the British market. Similar methods are employed in Jamaica. The fruit is official in modern pharmacopœia as a laxative and refrigerant.

MACOPA

EUGENIA JAVANICA Lam. Plate X, fig. 1. MACOPA, MACÚPA, T. V. Il.

A medium-sized tree with oblong-ovate, glossy leaves; open panicles of few, rather large, pink or white flowers; and turbinate, pink, fleshy fruits about 4 centimeters in diameter. Malaya.

The macopa is one of the most attractive appearing fruits found in the market, but the pulp is tasteless and fluffy. Slight importance.

MANGOSTEEN

GARCINIA MANGOSTANA L. Plate X, fig. 2. MANGOSTAN; MÁNGGIS, Jolo.

A medium-sized tree with oblong, coriaceous leaves and axillary flowers. Fruits globose, 5 to 6 centimeters in diameter; the persistent calyx reflexed; the pericarp rather brittle, purple; the pulp free, white or translucent, in about 5 nearly free segments usually only one of which contains a seed. Malaya.

The mangosteen thrives only in the southern islands, and the fruit reaches the Manila market in small quantities. It is famed as one of the most delicious fruits grown in the Tropics, perhaps in the world. The very juicy white pulp has a flavor partaking of strawberry or grape, and is the only edible part. It is easily removed from the thick purple rind, and resembles in shape a small tangerine orange. Unfortunately, it cannot be transported even with modern cold storage or when coated with wax, as the white pulp rapidly melts and turns brown. The seeds contain about 3 per cent of a valuable oil known as "cocum" or "kokam butter," which is used extensively in India. The thick purple rind contains tannin, resin, and mangostin, the last a yellow crystalline compound with medicinal properties. The dried rind or entire fruit is included in the pharmacopœia of India, and is much used as an astringent.

IBA

CICCA DISTICHA L. Plate XI, fig. 1. IBA, T; OTAHEITE or STAR GOOSEBERRY.

A small tree, the pinnately arranged leaves borne at the ends of the branches, the flowers very small, racemose, the racemes fascicled along the branches below the leaves. Fruits globose, pale green, about 1.5 centimeters in diameter, the pulp firm, acid, surrounding the hard stone. Tropical Asia.

The small fruits of the iba are very juicy, and are eaten raw, pickled, or cooked with sugar. When properly preserved, they resemble the gooseberry. Of slight importance.

GUAVA

PSIDIUM GUAJAVA L. Plate XI, fig. 2. GUAYÁBO, Sp.; BAYABAS, Il. T.

A shrub or small tree with ovate leaves and axillary, pedicelled, medium-sized white flowers. Fruit ovoid or globose to pyriform, smooth, green to pale yellow, 3 to 5 centimeters in diameter; the pulp pink or yellowish, containing numerous, small hard seeds. Tropical America.

The guava is used largely in the form of jelly, the excellence of which is too well known to require comment. The unripe fruit and bark, especially of the root, are astringent and of some slight importance medicinally.

SANTOL ·

SANDORICUM KOETJAPE (Burm.) Merr. (*S. indicum* Cav.) Plate XII, fig. 1. SANTOL, T. V. Il.

A medium-sized tree with trifoliolate leaves, the leaflets rather large, paniculate; pale yellow flowers; and globose yellowish fruit about 5 centimeters in diameter, the pericarp thick; the few large seeds surrounded by a translucent, soft, white, fibrous pulp. Malaya.

The santol is well known in all parts of the Islands, and eaten to a large extent. The pericarp is peeled and eaten raw, or cooked with sugar and candied to make "santol-paste." The pulp is strongly acid and difficult to remove from the large seeds.

CHICO MAMEY

LUCUMA MAMMOSA Gaertn. Plate XII, fig. 2. CHÍCO MAMÉY, MAMÉY, T.

A medium-sized tree with milky juice, lanceolate leaves, and axillary flowers. Fruit ellipsoid, brown, 15 to 20 centimeters long, containing a single very large seed. Tropical America.

The chíco-maméy is uncommon in the Philippines, growing only in isolated localities, and rarely reaching the market. The pulp is soft, has a sweet taste resembling a pear, and it suitable for marmalade, etc. It is justly celebrated in the West Indies, and should be cultivated here.

DATILES

MUNTINGIA CALABURA L. DATILES, RATILES, CEREZAS, MANZANITAS.

A small tree with ovate, somewhat viscid leaves, the flowers axillary, solitary, white, long-pedicelled. Fruit globose, red, 1 to 1.5 centimeters in diameter, very sweet, the soft pulp containing innumerable minute seeds. Tropical America.

The datiles grows abundantly, and is eaten largely by children. It is of minor importance.

LANZONE

LANSIUM DOMESTICUM Jack. Plate XIV, fig. 1. LANSÓNE, T. Il.; BÓBOA, V.

A small tree with pinnate leaves, the flowers small, borne in short racemes on the trunk and larger branches. Fruits ellip-

soid, about 3 centimeters long; the pericarp thin, pale-yellowish, tough, with some milky juice; the pulp white or translucent, watery; in 5 nearly free segments, only one of which usually contains a seed. Malaya.

The lanzone is an excellent fruit growing in grape-like clusters. The outer skin is rich in tannin and very bitter, but the creamy white pulp is sweet and slightly aromatic. The edible part resembles a small orange in shape and appearance, and is eaten by both Europeans and Filipinos.

DURIAN

DURIO ZIBETHINUS L. Plate XIII, figs. 1 and 2. DURIAN, CIVET, CAT FRUIT; DULIAN (*Moro*).

A tall tree with elliptic-oblong leaves, which are minutely scaly beneath; rather large, fascicled flowers borne on the trunk and branches; and large, ovoid fruits 20 to 30 centimeters long; the pericarp woody, covered with strong, sharp, pyramidal spines, splitting into 5 valves; the large seeds surrounded by the cream colored, soft, rank-scented pulp. Malay Archipelago.

The durian is abundant in parts of Mindanao and the islands of the Sulu Archipelago. During the season from May to September it is very plentiful in Jolo and Tawi-Tawi, selling at prices ranging from 10 to 40 centavos per fruit.

It is spoken of with contempt by most Europeans, and extolled as the "Emperor of Fruits" by Wallace, who considered that "eating durians is a sensation worth a voyage to the East." The creamy pulp is highly prized by the Malays and other Orientals. The odor is difficult to describe, but may be said to resemble decayed onions. The fruit is very nutritious, and is undoubtedly a valuable food among people who have overcome their objection to the fetid odor. The high percentage of a carbohydrate resembling erythro-dextrine adds to the food value. This is present in small granules that give a clear red with iodine.

CATMON

DILLENIA PHILIPPINENSIS Rolfe. Plate XIV, fig. 2. CATMÓN, T. V.

A medium-sized tree with elliptic, prominently nerved leaves; very large white flowers, and globose, acid, green fruit. Fruits about 5 centimeters in diameter, closely covered by the imbricate, thickened, fleshy sepals, the pulp arranged in a close spiral. Indigenous.

Catmon is plentiful in many parts of the Philippines, but seldom reaches the Manila market. The heavy green sepals are discarded, showing a light green pulp surmounted with pink

filaments.   The fruit is rather acid, and may be cooked with sugar as a vegetable resembling apple sauce.   The tannin content, especially of the unripe fruit, is rather high.   Other uses similar to tamarind pulp.

CONDOL

BENINCASA HISPIDA Cogn.   Plate XV, fig. 1.   CODÓL, T. V.; TANCUY, Il.

An annual, herbaceous, tendril-bearing vine with coarse large leaves and large, yellow, solitary flowers.   Fruit a pepo, ellipsoid, glaucous, about 30 centimeters long; the pericarp firm; the seeds borne in the center, numerous.   Tropical Asia.

Condol is cooked in thick sirup and allowed to dry, giving a popular sweetmeat.   The fruit is never eaten raw, as the white fluffy pulp has little taste and is unattractive.

CIRIHUELAS

SPONDIAS PURPUREA L.   Plate XV, fig. 2.   CIRULLAS, SIRIHUÉLAS, T.; SPANISH PRUNE, HOG PLUM.

A gnarled deciduous tree, the leaves pinnate, the flowers very small, purplish, appearing before the leaves.   Fruit subellipsoid, smooth, about 3 centimeters long, purplish, the pulp scant, yellowish, surrounding the single large stone-like seeds.   Tropical America.

The skin is thick, and the scant pulp possesses a peculiar sweetish taste.   The fruit is sold in considerable amount during the ·season, and is eaten largely by children.   Unimportant.

BIGNAY

ANTIDESMA BUNIUS Spreng.   Plate XVI, fig. 1.

A diœcious tree, 4 to 10 meters high, quite glabrous.   Leaves simple, glossy, 8 to 20 centimeters long, the spikes of small flowers terminal or axillary, simple, slender, 5 to 15 centimeters long.   Flowers greenish, numerous.   Fruit, when fresh, globose or ovoid, red, acid, edible, about 8 millimeters long; when dry, compressed and wrinkled, borne in rather dense cylindric spikes.

The fruit is plentiful in all parts, and is eaten with fish for its agreeable acid flavor.

TABLE III.—*Analyses of Philippine fruits.*

Name	Average weight of fruit	Edible portion	Seed	Skin	Total solids	Insoluble solids	Protein	Ash		Sugar				Polarization				Acidity				Sugar ratio
								Total	Alkalinity as K_2CO_3	Reducing	Sucrose by reduction	Sucrose by polarization	Total as invert	Direct	Invert	Temperature	Invert at 87°C	As sulphuric	Citric	Malic	Tartaric	
	Grams.	P. ct.												°V.	°V.	°C.	°V.	P. ct.				
Carabao mango	240	73	14	11	17.2	2.6	0.22	0.45	0.40	4.22	8.57	8.49	13.24	+3.0	-7.9	28	-3.3	0.14	0.18			95
Carabao mango, green [a]	175	70	10	20	13.7	2.8	0.38	0.25	0.17	1.12	0.74	1.10	1.90	-1.2	-2.6	31	-1.4	3.75	4.90			1
Pico mango	230	73	15	12	23.6	2.8	0.75	0.40	0.37	3.60	14.06	14.52	18.40	+9.2	-9.2	32	-3.8	0.23	0.30			80
Pahutan mango	85	60	22	18	25.7	8.1	1.12	0.53	0.39	2.00	14.76	14.78	17.54	+12.2	-6.6	31	-1.6	0.25	0.32			70
Chico	50	85	2	13	27.5	11.2	0.51	0.63	0.40	9.38	4.33	4.37	13.94	+2.3	-3.3	29	+0.2	0.05		0.07		279
Jak	8,000	25	10	65	34.4	3.1	0.42	1.23	0.90	8.28	14.17	13.92	22.98	+12.0	-5.7	31	-1.4	0.13		0.19		176
Casoy	88	90	6	4	14.0	2.5	0.71	0.37	0.24	10.28	0.12	0.31	10.41	-2.5	-2.9	30	-0.4	0.23		0.32		45
Guayabano	650	69	8	23	22.6	3.4	0.38	0.85	0.65	10.80	7.65	7.72	18.80	+4.6	-5.2	32	-0.8	0.74		1.04		25
Ates	240	52	6	42	25.0	3.1	1.12	0.97	0.85	15.77	0.22	0.31	16.00	-3.8	-4.2	30	-0.3	0.15		0.21		107
Camias	16				5.3	1.6	0.61	0.40	0.27	2.21	0.00	0.00	2.21	-0.8	-0.8	28	-0.6	1.20				18
Bilimbi	33				9.4	2.6	0.84	0.51	0.33	2.64	0.00	0.00	2.64	-1.5	-1.5	30	-1.1	0.24				11
Pineapple	800	50		50	13.8	2.1	0.44	0.36	0.32	3.36	5.74	5.82	9.41	+5.2	-2.2	31	-0.6	0.60	0.79			16
Limoncito	0.8	80	20		19.2	1.9	1.40	1.05	0.84	4.90	0.00	0.00	4.90	+1.6	+1.6	29	0.0	0.10		0.14		49
Pomelo	930	61	5	34	12.3	2.6	0.66	0.63	0.44	2.56	6.26	6.24	9.15	+5.4	-2.6	29		0.81	1.06			11
Papaya, female	1,350	47	9	44	10.5	1.6	0.44	0.58	0.52	5.88	0.08	0.05	5.97	-0.7	-0.7	31	0.0	0.11	0.14			54
Papaya, hermaphrodite	900	63	7	30	10.4	1.5	0.50	0.51	0.42	5.82	0.07	0.05	5.90	+0.6	-0.7	31	0.0	0.12	0.15			49
Melon	770	75	10	15	5.2	0.8	0.24	0.52	0.36	2.39	0.37	0.37	3.31	+0.3	-0.8	28	-1.0	0.08	0.11			31
Melon español	700	77	13	13	4.0	0.7	0.80	0.50	0.35	1.24	0.60	0.53	1.87	+0.2	-0.9	29	-0.2	0.13	0.16			12
Watermelon	2,250	51	4	45	8.7	0.4	0.60	0.18	0.12	5.73	1.25	1.32	7.04	+2.4	-4.1	28	-0.7	0.02	0.06			352
Mabolo	300	55	30	15	23.2	6.9	0.75	0.88	0.74	6.90	4.57	4.71	10.83	+2.0	-4.0	31	-0.6	0.11		0.16		99
Duhat	4	75	25		19.2	3.5	0.81	0.70	0.67	12.70	0.00	0.00	12.70	+3.5	-3.4	28	-0.9	0.63		0.88		20
Tamarind, ripe pulp	4	50	50		82.2	8.8	3.00	3.16	2.80	40.20	0.91	0.94	41.20	+3.2	-4.4	31	+4.4	9.36			15.33	4

	15	100			85.0	10.1	1.41	4.21	3.90	0.00	0.00	0.00	00.00					2.60		3.98
Tamarind, green	15	100	---	---	---	10.1	1.41	4.21	3.90	0.00	0.00	0.00	00.00	---	---	---	---	2.60	---	3.98
Macopa	30	90	8	2	8.6	1.9	0.50	0.27	0.18	6.56	0.00	0.00	6.56	2.1	-2.1	29	-0.8	0.17	0.15	38
Mangosteen	100	31	2	67	19.8	1.9	0.50	0.23	0.20	4.20	12.62	12.63	17.48	+11.6	-4.4	32	-1.4	0.37	0.49	47
Iba	1.5	---	---	---	11.0	1.2	0.94	0.57	0.35	4.16	0.63	0.78	4.82	-1.4	-2.4	30	-0.6	1.30	1.84	4
Guava	45	83	---	17	24.2	16.0	1.38	0.71	0.56	3.34	3.99	3.63	7.64	+1.8	-2.8	32	-2.0	0.32	0.42	23
Santol	85	70	5	25	20.3	6.4	0.86	0.98	0.49	3.08	1.72	1.66	4.89	+0.8	-1.3	32	0.0	1.08	1.35	5
Chico mamey	500	70	16	14	31.2	9.7	1.23	1.26	0.83	8.52	8.15	8.00	17.10	+9.5	-0.8	28	-1.3	0.14	0.18	122
Datiles	1.5	80	---	20	24.6	8.4	1.98	0.80	0.67	8.05	5.17	5.34	13.49	+2.4	-4.4	31	-0.6	0.05	---	269
Lanzone	20	80	6	14	19.9	1.6	1.13	0.59	0.45	4.90	8.10	8.01	13.42	+5.8	-4.4	29	-1.0	0.77	1.00	17
Durian [b]	2,250	30	15	55	44.5	---	2.31	1.24	0.98	4.79	8.76	8.97	14.01	+12.8	+1.3	30	+6.3	0.13	0.19	100
Catmon	62	38	---	62	8.1	3.8	0.25	0.30	0.25	2.35	0.08	0.23	2.38	-0.6	-0.9	30	0.0	1.08	1.52	2
Condol	900	90	---	10	5.0	2.0	0.69	0.40	0.26	2.09	0.26	0.54	2.36	-0.4	-1.1	30	0.0	0.05	0.07	47
Cirihuelas	20	50	23	27	13.0	4.3	0.63	0.27	0.19	8.08	6.14	5.97	14.54	+5.4	-2.2	31	-1.0	0.35	0.53	42
Bignay	0.3	80	20	---	5.2	---	0.75	0.78	0.67	0.00	0.00	0.00	0.00	---	---	---	---	2.13	2.78	---

[a] Starch content = 3.9.   [b] Starch content = 11.1.

ILLUSTRATIONS

(Photographs by Martin)

PLATE I

FIG. 1. Carabao mango (*Mangifera indica* L.).
2. Pico mango (*Mangifera indica* L.).

PLATE II

FIG. 1. Pahutan mango (*Mangifera indica* L.).
2. Chico (*Achras sapota* L.)

PLATE III

FIG. 1. Jak fruit (*Artocarpus integrifolia* L. f.).
2. Breadfruit (*Artocarpus communis* Forst.; A. *camansi* Blanco).

PLATE IV

FIG. 1. Casoy (*Anacardium occidentale* L.).
2. Guayabano (*Anona muricata* L.).

PLATE V

FIG. 1. Ates (*Anona squamosa* L.).
2. Camias (*Averrhoa bilimbi* L.).

PLATE VI

FIG. 1. Bilimbi (*Averrhoa carambola* L.).
2. Pomelo (*Citrus decumana* Murr.).

PLATE VII

FIG. 1. Papaya (*Carica papaya* L.).
2. Melon (*Cucumis melo* L.).

PLATE VIII

FIG. 1. Melon español (*Cucumis melo* L.).
2. Watermelon (*Citrullus vulgaris* Schrad.).

PLATE IX

FIG. 1. Mabolo (*Diospyros discolor* Willd.).
2. Duhat (*Eugenia jambolana* Lam.).

PLATE X

FIG. 1. Macopa (*Eugenia javanica* Lam.).
2. Mangosteen (*Garcinia mangostana* L.)

PLATE XI

FIG. 1. Iba (*Cicca disticha* L.).
2. Guava (*Psidium guajava* L.).

PLATE XII

FIG. 1. Santol [*Sandoricum koetjape* (Burm.) Merr.].
2. Chico mamey (*Lucuma mammosa* Gaertn.).

PLATE XIII

FIG. 1. Durian (*Durio zibethinus* L.).
2. Same as above.

PLATE XIV

FIG. 1. Lanzone (*Lansium domesticum* Jack).
2. Catmon (*Dillenia philippinensis* Rolfe).

PLATE XV

FIG. 1. Condol (*Benincasa hispida* Cogn.).
2. Cirihuelas (*Spondias purpurea* L.).

PLATE XVI

FIG. 1. Bignay (*Antidesma bunius* Spreng.).
2. Tamarind (*Tamarindus indica* L.).

5 cm.

Fig. 1.   Carabao mango (Mangifera indica L.).

5 cm.
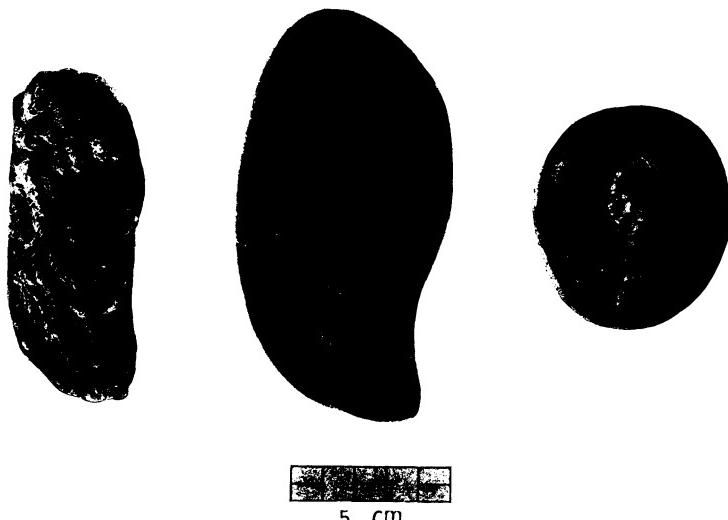
Fig. 2.   Pico mango (Mangifera indica L.).

PLATE I.

5 cm.

Fig. 1.   Pahutan mango (Mangifera indica L.).


5 cm.
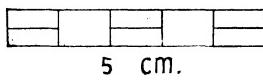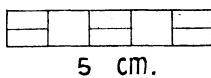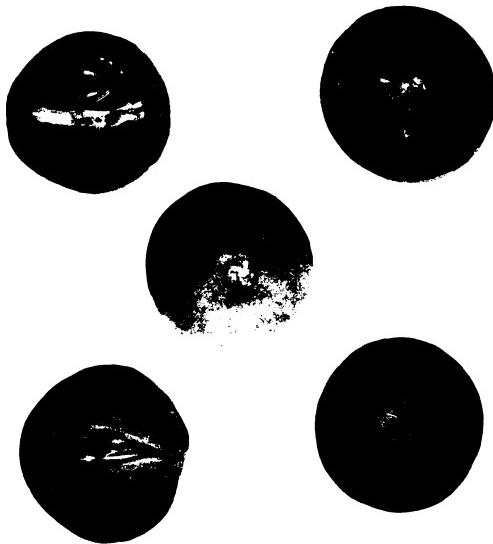
Fig. 2.   Chico (Achras sapota L.).

PLATE II.

10 CM.
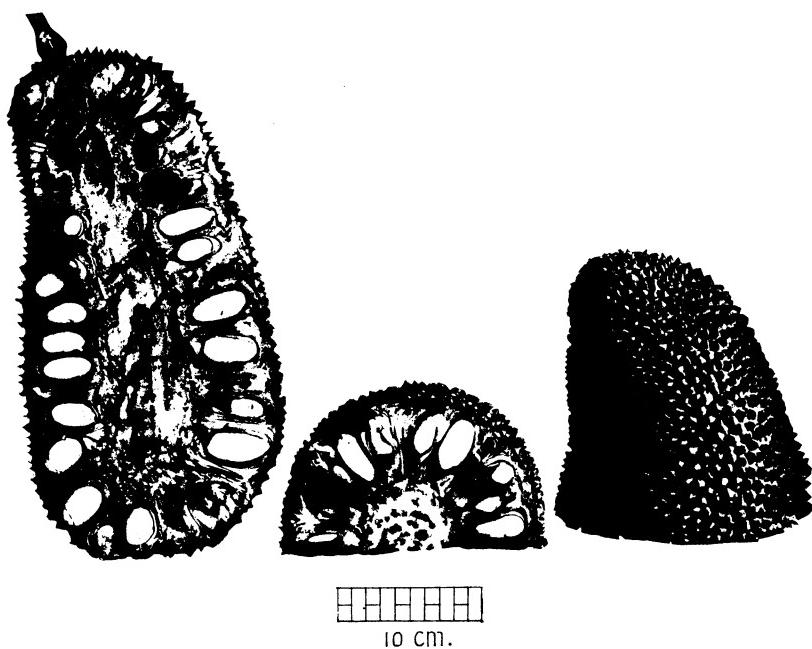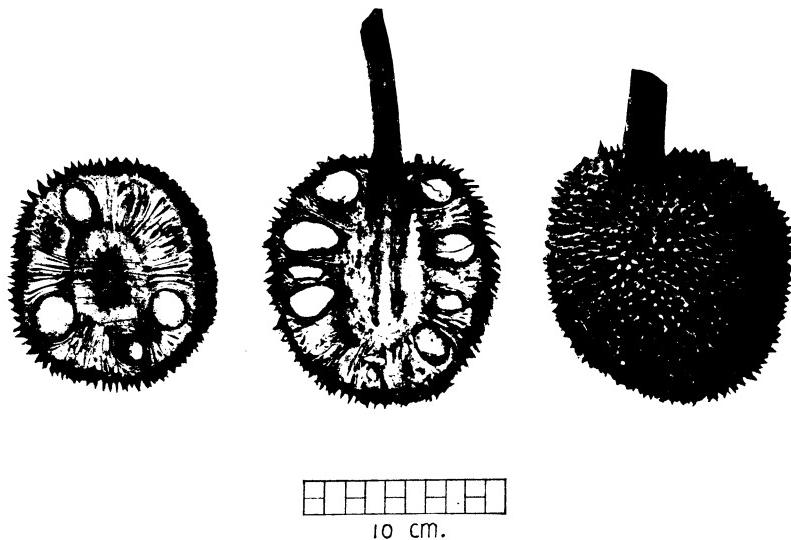
Fig. 1. Jak fruit (Artocarpus integrifolia L. f.).

10 CM.

Fig. 2. Breadfruit (Artocarpus communis Forst.; A. camansi Blanco).
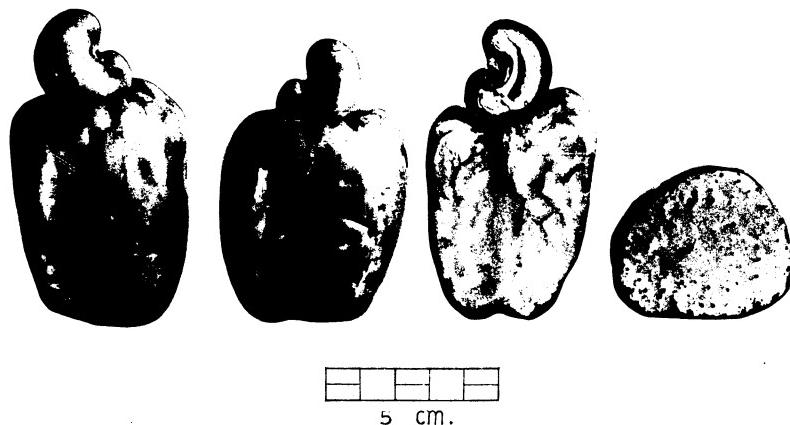
PLATE III.

5 cm.

Fig. 1.   Casoy (Anacardium occidentale L.).

5 cm.

Fig. 2.   Guayabano (Anona muricata L.).

PLATE IV.

5 cm.

Fig. 1. Ates (Anona squamosa L.).

5 cm.
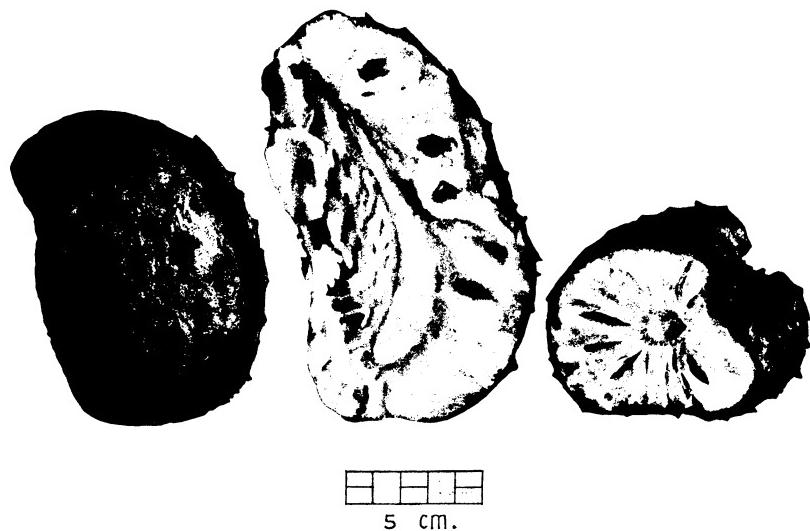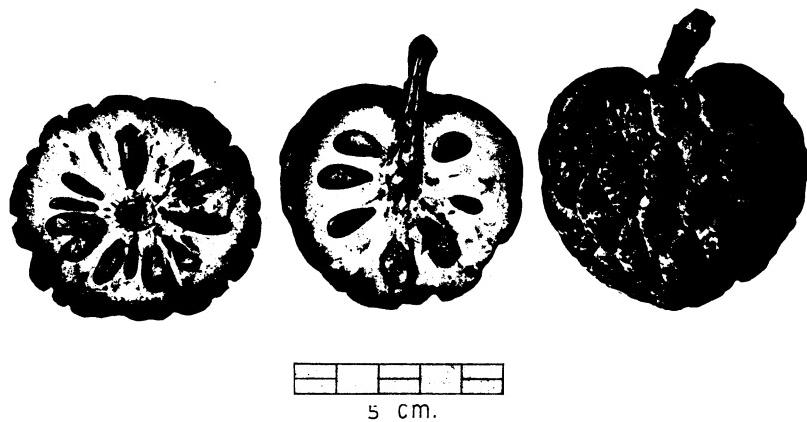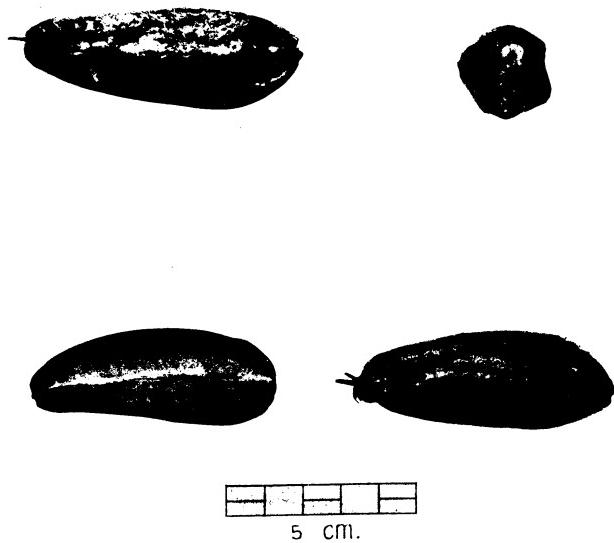
Fig. 2. Camias (Averrhoa bilimbi L.).

PLATE V.

5 cm.
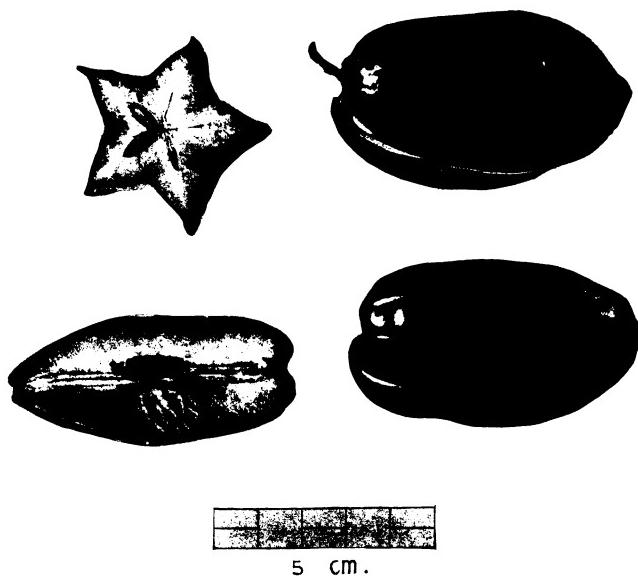
Fig. 1.   Bilimbi (Averrhoa carambola L.).
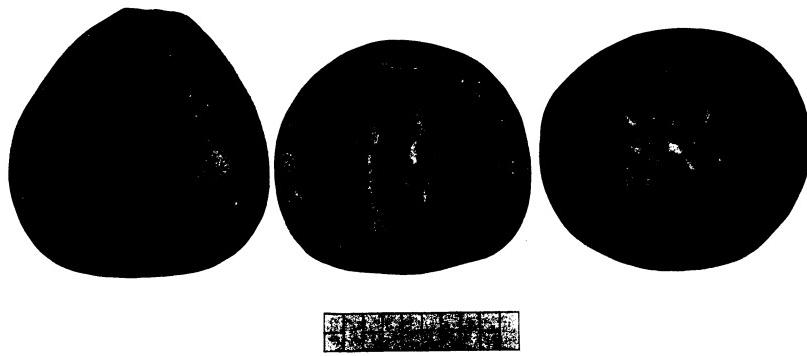
10 cm.

Fig. 2.   Pomelo (Citrus decumana Murr.).

PLATE VI.
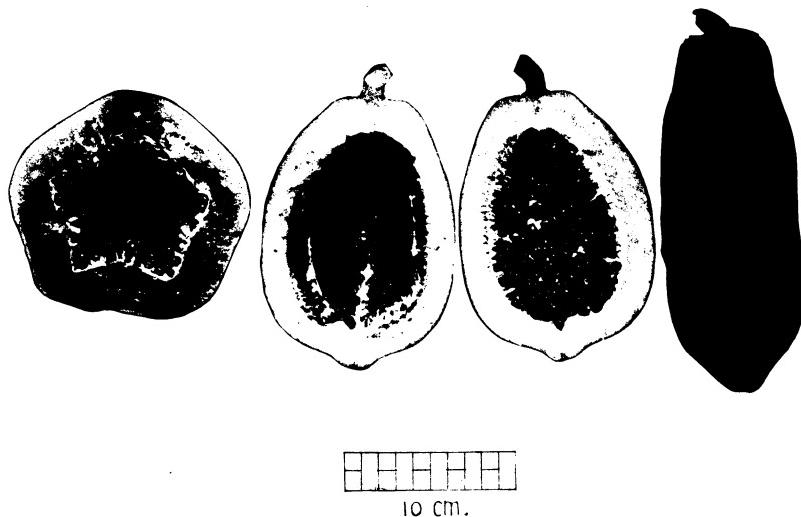
10 cm.

Fig. 1.   Papaya (Carica papaya L.).
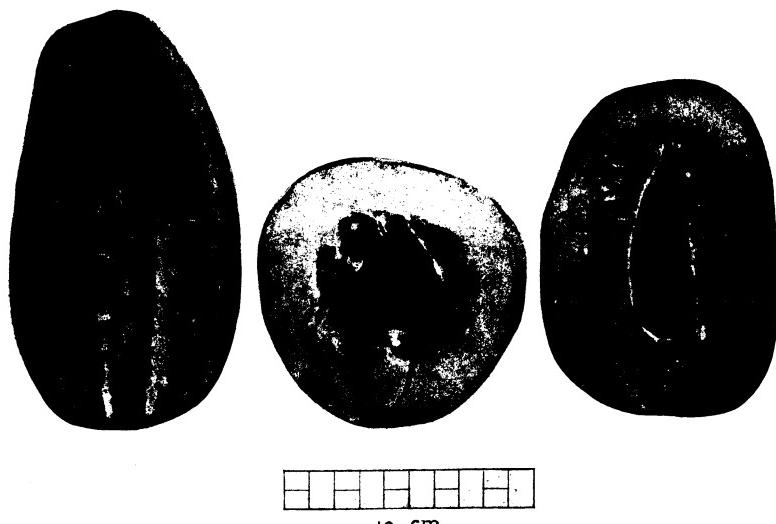
10 cm.

Fig. 2.   Melon (Cucumis melo L.).

PLATE VII.
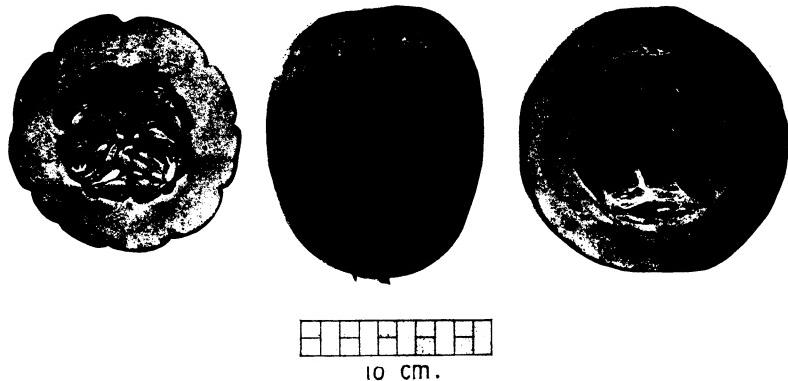
IO cm.

Fig. 1.   Melon español (Cucumis melo L.).
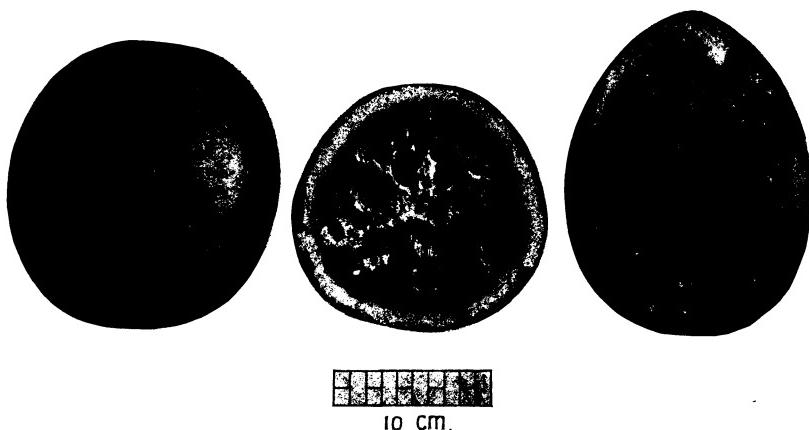
IO cm.

Fig. 2.   Watermelon (Citrullus vulgaris Schrad.).

PLATE VIII.

5 cm.

Fig. 1.   Mabolo (Diospyros discolor Willd.).

3 cm.
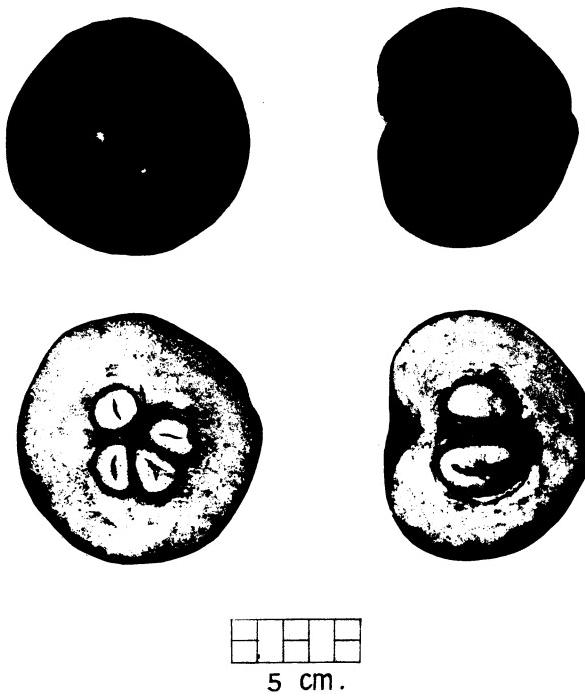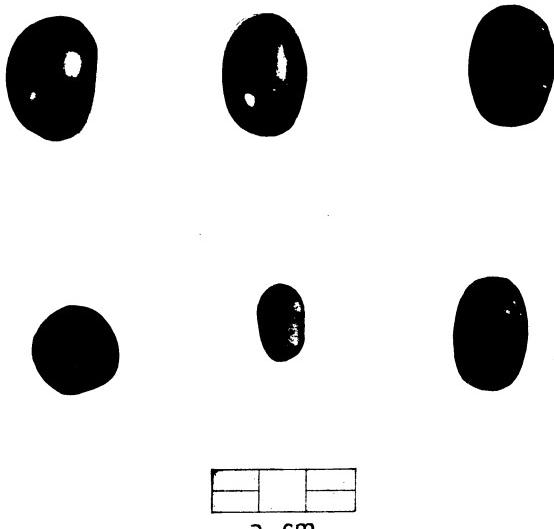
Fig. 2.   Duhat (Eugenia jambolana Lam.).

PLATE IX.

5 cm.
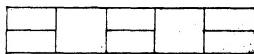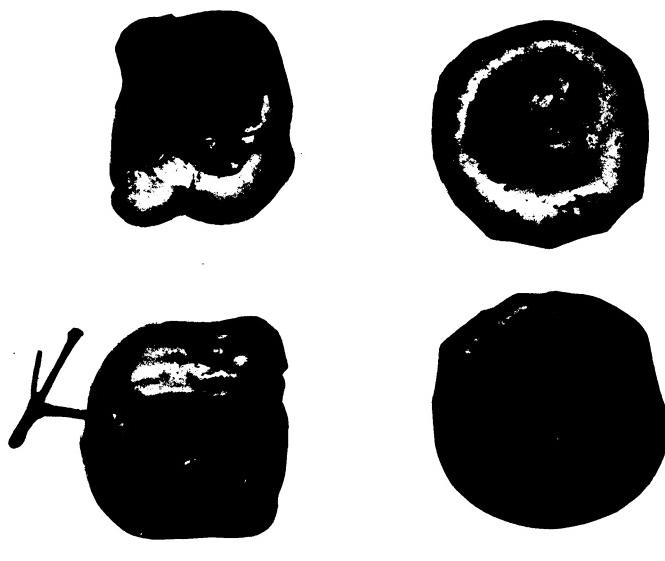
Fig. 1.   Macopa (Eugenia javanica Lam.).

5 cm.
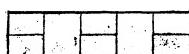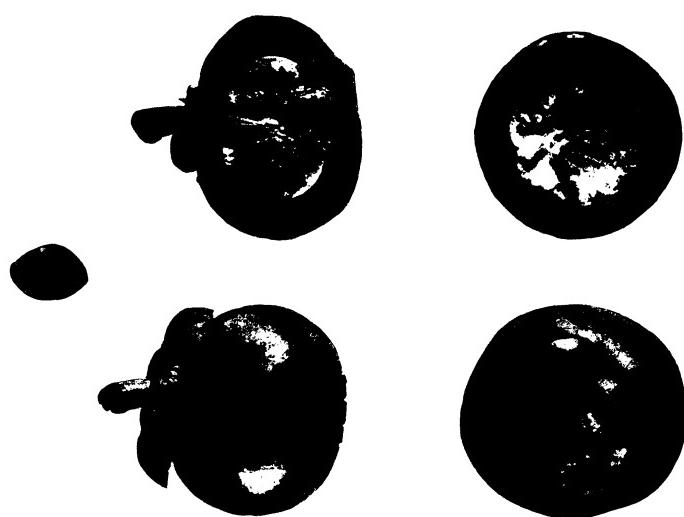
Fig. 2.   Mangosteen (Garcini mangostana L.).

PLATE X.
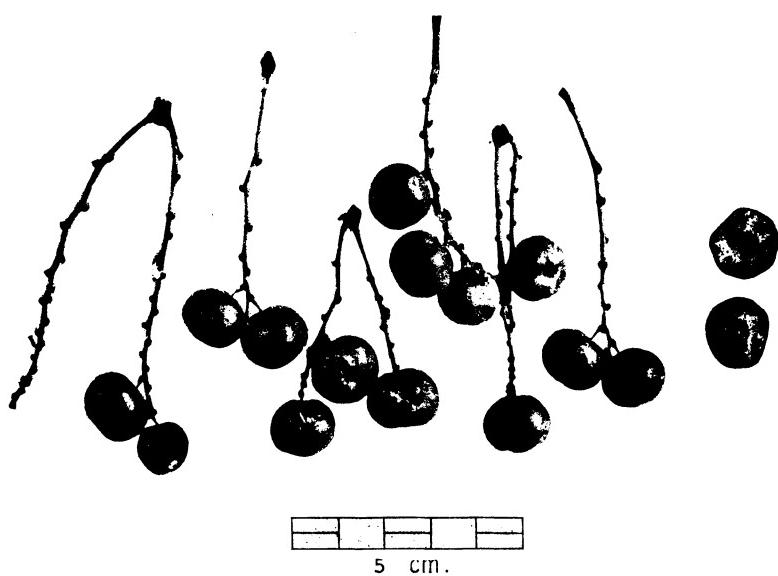
Fig. 1.   Iba (Cicca disticha L.).
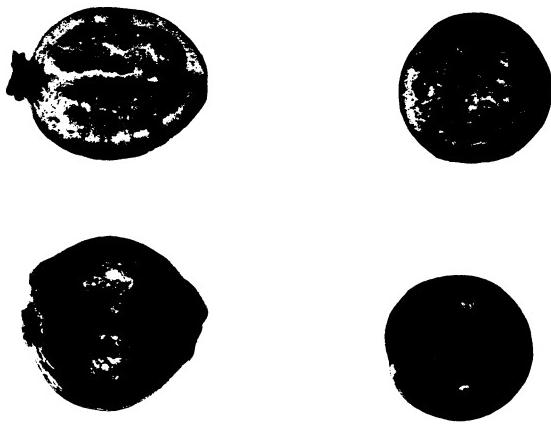
Fig. 2.   Guava (Psidium guajava L.).

PLATE XI.

5 cm.

Fig. 1.   Santol (Sandoricum koetjape (Burm.) Merr.

10 cm.
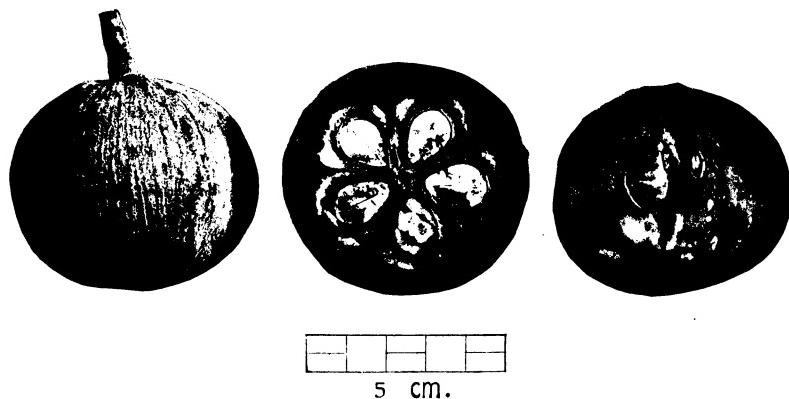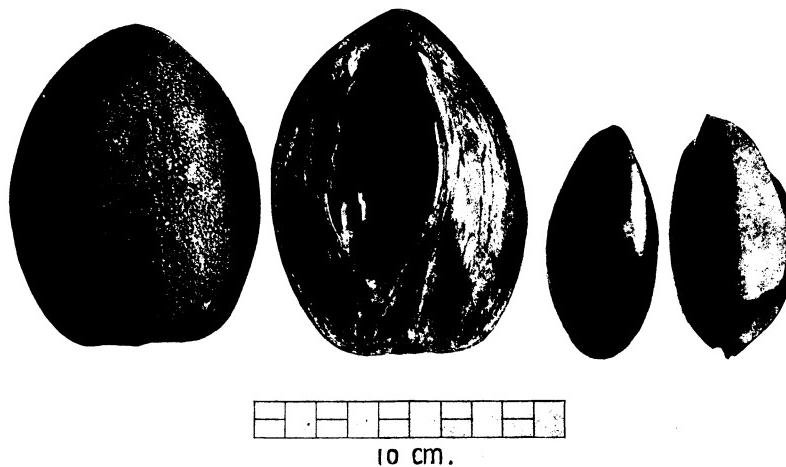
Fig. 2.   Chico mamey (Lucuma mammosa Gaertn.).

PLATE XII.

10 cm.

Fig. 1.   Durian (Durio zibethinus L.).

10 cm.
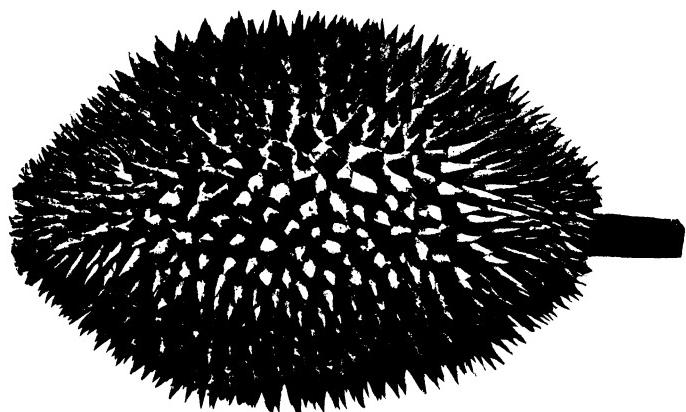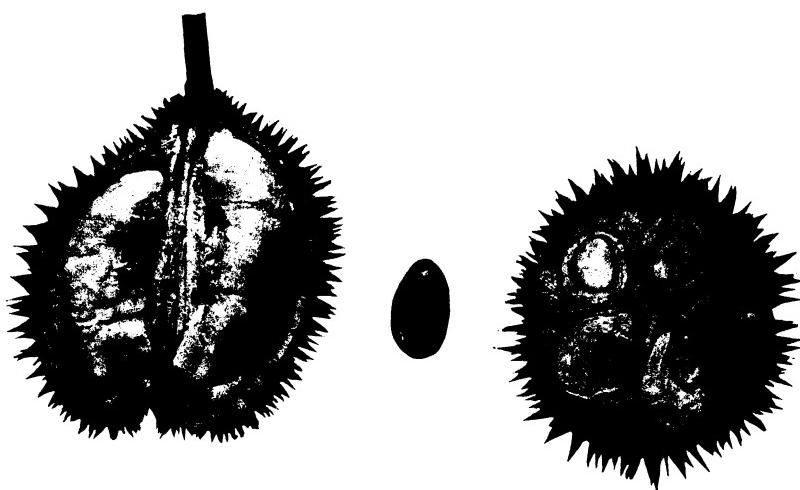
Fig. 2.   Durian (Durio zibethinus L.).

PLATE XIII.

5 cm.

Fig. 1.   Lanzone (Lansium domesticum Jack).

5 cm.
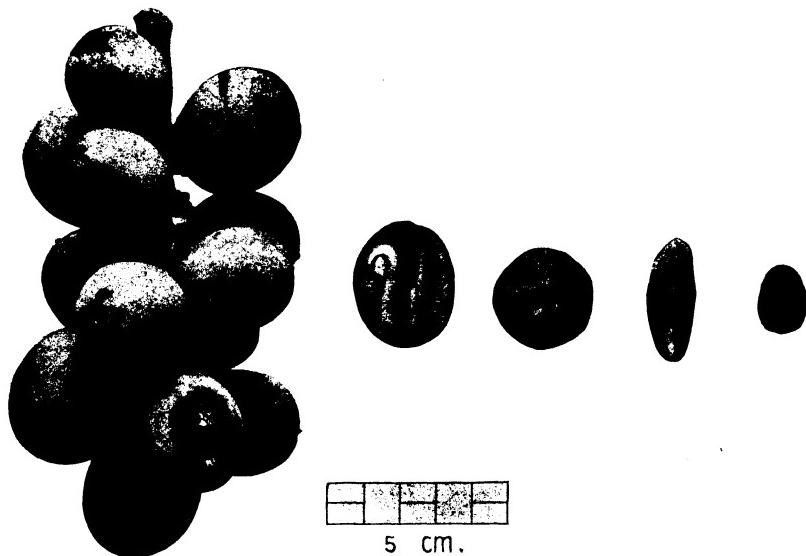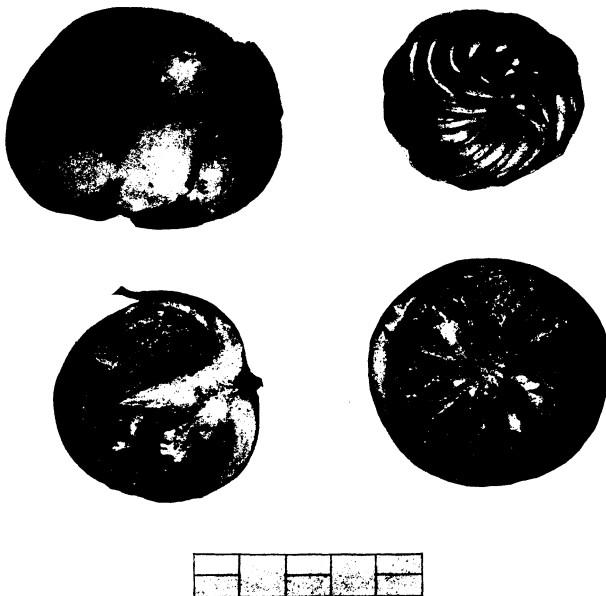
Fig. 2.   Catmon (Dillenia philippinensis Rolfe).
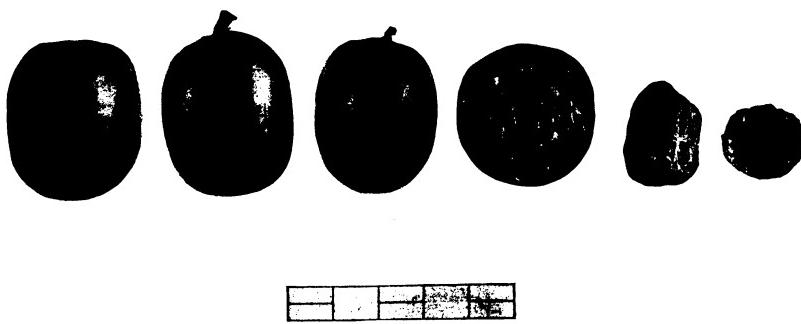
PLATE XIV.

10 cm.

Fig. 1.   Condol (Benincasa hispida Cogn.).

5 cm.

Fig. 2.   Cirihuelas (Spondias purpurea L.).
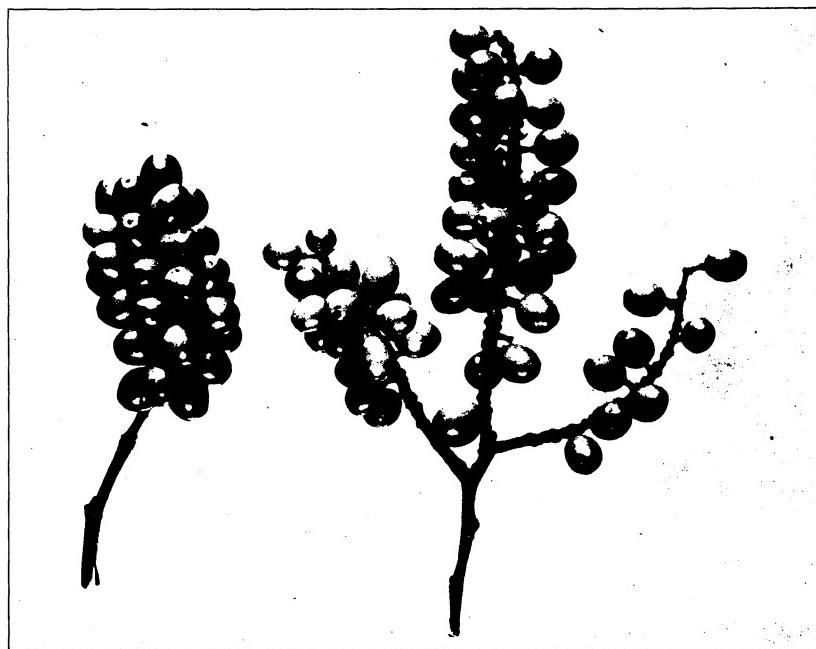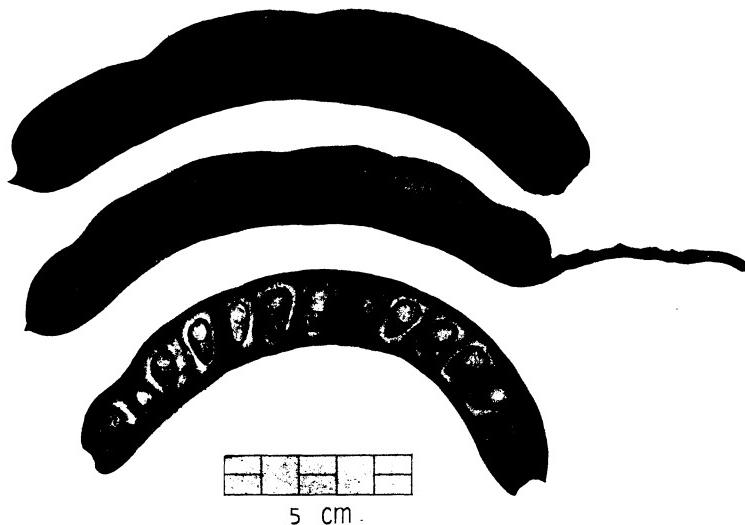
PLATE XV.

Fig. 1.   Bignay (Antidesma bunius Spreng.).

5 cm.

Fig. 2.   Tamarind (Tamarindus indica L.).

PLATE XVI.

ORE DEPOSITS OF THE PHILIPPINE ISLANDS

By F. T. EDDINGFIELD

(*From the Division of Mines, Bureau of Science, Manila, P. I.*)

Three plates and 4 text figures

The discussion of the genesis of the ore deposits of the Philippines is handicapped by the lack of sufficient data in regard to primary ore. Mining is in its infancy, and most of the operations of mining and development have been carried on wholly in the zone of oxidation. This is particularly true of those deposits which represent the most important gold ores; that is, those made up of manganese, calcite, and quartz, and of manganese and quartz alone. However, conditions of a somewhat exceptional nature are encountered which present opportunities for discussion. These are, mainly, the comparative youth of the rock formations, the evidence of volcanic activity throughout the Islands, the abundance of mineral springs, the unusually large number of veins within a limited area, and the association of manganese, calcite, and quartz in many of the mineral deposits.

GEOLOGY

The rocks of the Philippine Islands for the most part are of Tertiary or post-Tertiary age. Very few have been found

which can be provisionally classed as pre-Tertiary.   These are
tabulated by Smith [1] as follows:

Radiolarian chert	Ilocos Norte.
Quartz porphyry	Lepanto.
Diorites	Benguet.
Gabbros	Leyte.
Pyroxenite	Ilocos Norte.
Peridotite	Near Olongapo.

No definite evidence is advanced to confirm this classification,
and while it seems probable that the majority of these rocks are
pre-Tertiary, it is also probable that some of the intrusions
of quartz diorite were of later geologic age or had suffered indi-
vidual uplifts which thrust the diorite alone through the sedi-
mentaries or igneous rocks which had previously overlain it.

One of the above two conditions may have existed in Cebu as
shown by the geologic section by Smith [2] where the igneous in-
trusion seems to have folded the sedimentaries, and also in
Batangas as shown by the geologic section by Smith.[3]   The quartz
diorite in the Aroroy district, Masbate, has been discussed by
Ferguson.[4]   It is found intrusive in the Kaal series of sedi-
mentaries, which, on account of lack of definite evidence to the
contrary, should be classed as Tertiary, since no pre-Tertiary
sediments have ever been found in the Philippines.

Masses of rock similar in appearance to the diorite, but in
places slightly porphyritic, are found intruded into the andesite
in Gold Creek near the Muyot, Major, and Ascension mines,
and in Bued River Valley, Benguet.   This rock megascopically
is quite distinct from the andesite, but is with difficulty differ-
entiated from the diorite intrusions to the east.   It is much
lighter in color than the andesite, and the contacts between
it and the andesite are very well marked.   Therefore, it would
appear that these intrusions were derived from the diorite
magma, but had cooled more quickly on account of their being
intruded as small masses.

In Paracale and in Suyoc we find granite gneiss and granite
having a relationship to the veins similar to the diorite in
Benguet and Aroroy.   The granite and the granite gneiss have
been provisionally located in the Tertiary.   Therefore, one would
be inclined to draw an analogy between the two classes of intru-
sives and to place them in the same geologic age.

[1] *This Journal, Sec. A* (1910), **5**, 319.
[2] *Loc. cit.*
[3] *This Journal* (1906), **1**, 635.
[4] *Ibid., Sec. A* (1911), **6**, 405.

VOLCANOES

At one time or another volcanoes have been exceedingly active in all parts of the Philippines as shown by the enormous deposits of volcanic tuff which in places are found to a depth of over 200 meters. The influence the volcano has had upon ore deposits is very uncertain. In examinations of mining districts throughout the world, we are confronted by numerous instances where the mineral district is in a section once the seat of volcanic action. This is true of Cripple Creek, Colorado, and numerous other prominent localities in Nevada, Utah, Montana, Arizona, and New Mexico. T. A. Rickard[5] has discussed the Cripple Creek Volcano exhaustively, and in a closing paragraph emphasizes the influence it had upon ore deposits in the district, principally by producing conditions in the rock favorable to ore deposition. Francis Church Lincoln[6] has stated that the mineral constituents of volcanic emanations have been shown to include all the economic metals, with the exception of gold and silver, and that silver was found in galena in ejected marble blocks of Monte Somma. It has also been noted that among the products in the fumaroles ejected are such active agents as hydrochloric acid, sulphuric acid, sulphurous anhydride, hydrogen disulphide, carbon dioxide, sulphur, hydrofluoric acid, and hydrobromic acid.

If it be considered that the fracturing of the rocks and the creation of the fissures have resulted directly from the cooling of the molten rock at, or near, the surface of the earth, or from the eruptive force of the volcano and the subsequent subsidence of the nearby areas, it is evident that the most active agent lying beneath the fracture zone would be the molten or heated magma which produced the volcanic flows. The fissures would probably be the easiest means for the escape of the resulting gases or for the ascension of the solution which might subsequently be derived from the cooling mass. The neck of the volcano might in some cases also furnish an easy passage. Such a condition may have existed in the case cited by Kemp[7] of the Bassick mine, Custer County, Colorado, where the ore occurs in an old volcanic neck as a coating on the bowlders. That so few cases of this kind exist is due probably to the fact that the neck of the volcano solidifies in a confined space in which practically no

[5] *Trans. Am. Inst. Min. Eng.* (1900), **30**, 367.

[6] *Econom. Geol.* (1907), **2**, 265.

[7] Ore Deposits of the U. S. and Canada.   4th ed. New York and London (1901), 281.

fissuring takes place. It is evident that the active volcano would have little or no part in ore formation, since the magma below, in its extremely heated condition, would give off nothing but gas or molten rock, which would escape from the volcanic vent. Its chief agency is in the formation of fissures which are filled later by ascending mineral-bearing solutions, probably derived from, or influenced by, the same magma at a cooler stage.

MINERAL SPRINGS

Hot springs are abundant throughout the Islands. In some localities they have been found depositing arsenic, iron, lime, salt, or sulphur. In the Benguet mineral district, large masses of silica containing small values of gold have been found, which were undoubtedly deposited by springs. Silicification of certain rocks has taken place to a marked extent in this region, and has led to the name "Benguet formation" for this class of rock. It would appear that vein formation is still going on and that gold has recently been, or is at present being, deposited in the fissures up which the gold-bearing solutions are coming.

GOLD ORE VEINS

Gold-bearing veins are found filling fissures in andesite, andesite agglomerate, diorite, and granite gneiss, and also along the contacts between two classes of igneous and between igneous and sedimentary rocks. By far the greatest number of veins are found in the andesite. These fissures seem to have been formed without appreciable movement or vertical displacement, as shown by the absence of slickensides on the walls of the fissures and the comparative absence of faults in a region which must have undergone more than one period of fissuring.

The faulting of a quartz vein is seen in the "Tejon dike" on the Ascension group, Baguio, Benguet. This dike, or vein, and another or possibly the same vein in Emerald Creek have been faulted twice, as shown in fig. 1. One section of the vein has been entirely displaced, and the direction of strike of the western portion changed by about 30°. This faulting may have been due to a local shifting of the rock comparatively near the surface. The only other example, so far recorded, is on the Eastern property, Aroroy, where only one of a series of six or eight parallel veins is faulted and has a lateral displacement of about 3 meters. The fault line was perpendicular to the vein. It showed well-marked slickensides, and contained drag material from the
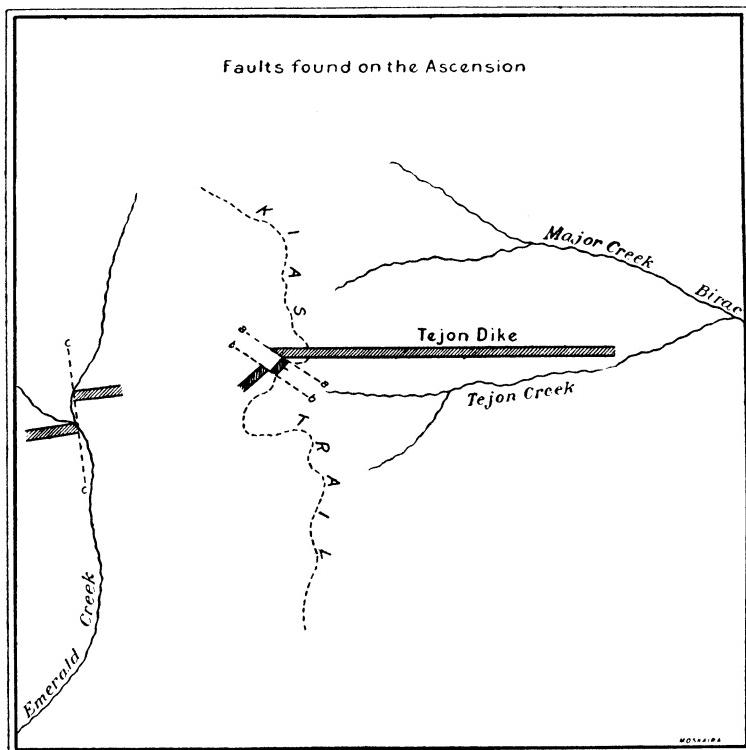
FIG. 1.—Showing faulting of the "Tejon dike" on the Ascension group.

vein. This case shows conclusively that at least two periods of fissuring occurred in this region.

The tendency toward parallel arrangement of fissuring is very marked in Aroroy and Paracale, but in Benguet there is little evidence of any regularity, except for a tendency toward east and west directions rather than north and south. A large number of long, strong veins strike almost due east and west, but the most promising veins, so far exploited, strike either northeast-southwest or northwest-southeast. In Aroroy the veins strike almost uniformly northwest-southeast, and in Paracale they strike northeast-southwest. This arrangement of fissures may have been produced by some force acting upon one portion only of the fracture zone. The simplest case would be the subsidence of one side or the elevation of the central portion of the area, thereby producing fissuring on a large scale similar to those on the crest of an anticline. However, in Baguio is found much more pronounced and irregular shattering of the rock, producing

in some places cross fissuring, which strongly suggests pressure fracturing.

In as much as mining has been done only comparatively near the surface, it is impossible to tell how deep the ore deposits can be expected to go. Depths from 30 to 100 meters have been explored, and at this depth no apparent decrease in width has been found. The fissures in general are strong, and can be traced for over 500 meters along the strike. In Mambulao it was noted that the veins in the granite gneiss were wide and strong, but where they passed from the gneiss to the schist they became very irregular, splitting into stringers, and finally pinched out entirely. In the San Mauricio mine the veins near the shaft in the schist, which overlies the gneiss at that point, are very irregular in dip and strike, but when the gneiss is reached with depth these veins are united into one uniform vein. This is probably due more to the physical condition of the schist than to chemical action. The schist offers great resistance to fissuring, except parallel to the planes of compression. This has resulted in a resistance to transverse fissuring and a tendency to change the fissure parallel to the schistosity.

In Benguet, the Fianza vein is either cut off at the diorite or the fissuring in the andesite does not extend into the diorite. In another section of Benguet on the Ascension group, a vein was found varying in width from 1 to 5 meters in a distance of 1 kilometer along the strike. These cases are the only ones so far found where marked irregularities occur, except in cases of lateral enrichment or in contact deposits between igneous and sedimentary rocks. These veins are small, unimportant, and presumably limited in extent. No veins are found cutting across sedimentaries.

VEIN FILLING

The difference in the mineralization of the veins of any one district is very marked, and indicates clearly that the ascending solutions must have taken up minerals from different formations in their path. It is apparent in Suyoc, Benguet, and in Aroroy that solutions from at least two different sources have produced most of the vein matter, each one dissolving different minerals in its ascent. At one period, solutions deposited silica, silica and manganese, silica and copper, or silica and lead, depending upon the minerals encountered in their passage. At another period, they deposited calcite and calcite and manganese. In

one case alternations of these two classes of solutions have taken place, producing banding of calcite and quartz. The country rock seems to have had but little chemical effect upon these deposits, and the predominance of veins in the andesite is due entirely to its more fractured condition.

The most characteristic feature in regard to the ore deposits of the Philippines is the abundance of quartz-calcite-manganese veins. Quartz-manganese veins are very common in Tertiary deposits of the United States, some of which also contain calcite, but the occurrence of large amounts of calcite associated with the quartz and manganese is unusual.

The primary manganese ore is probably either manganiferous calcite or rhodonite; in one mine rhodochrosite was found. It is probable that, where the manganese and quartz were deposited together, the primary ore would contain some alabandite. In the zone of oxidation are found the oxides, manganite, and wad. These oxides are found in streaks in the veins, and usually contain the highest gold values found in the deposit.

The characteristic section of this type of vein in the zone of oxidation consists of: (1) A band of solid compact calcite, varying in width from 0.5 to 6 meters, often lying next to the foot wall; (2) bands of black, soft manganese, usually mixed with quartz fragments or honeycomb quartz, and often containing pockets of white quartz crystals which in some mines indicate high values; these bands are found in some cases next to the calcite, in some cases next to the foot wall, and almost always next to the hanging wall; they vary in width from 0.2 to 4 meters; (3) a band of massive quartz, carrying sulphides and varying in width from 0.1 to 4 meters, usually separated from the calcite by a manganese band.

ALTERATION IN THE VEINS

Alteration has taken place in the veins due to oxidation, leaching, and enrichment. These elements have in some cases entirely changed the character of the ore above the lowest level of ground water, so that very little remains to indicate the true character of the primary ore.

The zone of oxidation in the veins in many cases is deep on account of the mountainous condition of the regions and the resulting low limit of ground-water level. The ground-water level varies from a plane near the surface during the rainy season to a plane near or possibly below the level of the bottom

of the valley, which drains the ore body, during the dry season. The variation is more than 100 meters in some cases. This tends to retard oxidation slightly during the rainy season, when the vein matter is so filled with water as to be protected from atmospheric influences, and also during the dry season, when the chemical activity of water is lacking. These extreme periods exist for only three or four months each year. During the remaining months there is moderate rainfall, which creates very favorable conditions for oxidation. The net result is probably much greater than in colder countries where surface waters are frozen for six or seven months.

The Philippines escape the destructive action of great changes in temperature, but since such action only affects the surface rock it has little bearing upon ore bodies in general. This is more than offset by the heavy rainfall, the humidity of the atmosphere, and, in veins, by the shattering due to earthquakes and earth movements. The temperature of the percolating waters, also, plays an important part in oxidation and hydrations, and the greater average temperature of the surface waters causes greater chemical activity.

The zone of oxidation extends from the surface to below the extreme lowest limit of ground-water level. Some of the veins are so shattered as to permit easy circulation of surface water, which causes almost complete oxidation throughout. This is also true of several veins in Baguio which, though but little shattered, are formed of granular, porous, or crystalline quartz which permits extensive circulation. Other veins made up of compact and shattered material or those in which channels are found along one or both walls, or through the veins, often contain unoxidized material even near the surface. The majority of the veins in Paracale are but little oxidized, due in part to the unshattered condition of the ore body, in part to the low relief of the district and to the consequent nearness to the surface of the permanent ground-water level. In Baguio, also, there are a few cases where unshattered quartz or calcite veins have resisted oxidizing agents.

Leaching has played an important part in the gold veins, but its effect has been one of enrichment rather than impoverishment. In practically all cases the richest ore is at or near the outcrop, and values decrease almost uniformly with depth. This is caused by: (1) Rapid erosion of impoverished material, (2)

leaching out of valueless minerals, (3) mechanical concentration of valuable minerals, and (4) chemical concentration of valuable minerals.

Owing to the steep slopes characteristic of most of the districts, the erosion of the outcrops of the veins is very rapid. During the rainy season, with its high ground-water level, only a small part of the vein is subject to rapid leaching. At the water level the leached values tend to be redeposited, forming a zone near the surface. A large part of the partially leached material above this level is washed away, and the gold content may eventually form placers. With the descending of the ground-water level, leaching action takes place extensively, and calcite, copper, iron, manganese, and other minerals are dissolved, and either flow away in solution or are redeposited lower down in the waterways.

The solubility of calcite is very great on account of the large amount of carbonic acid in the surface waters. This has been found to vary from 0.22 to 0.45 per cent by volume. Roth[8] states that 1 liter of pure water, either cold or boiling, will dissolve about 18 milligrams of calcium carbonate. Water saturated with carbonic acid will dissolve from 700 to 880 milligrams at 10°C.,[9] or about fifty times as much as pure water. This has proved an important factor in the leaching of the numerous calcite-bearing veins in the Philippines.

In the upper workings of the Colorado mine the ore is honeycomb quartz stained with iron and manganese, but no calcite has been found. However, the quartz in the vein shows perfect mold forms for calcite crystals of characteristic shape, and proves that at one time the vein contained a large percentage of calcite which was afterwards leached from most of the vein in the zone above average ground-water level.

In the Eastern mine, Aroroy, honeycomb quartz is also found, but in this mine calcite can be found very near the surface. The leaching has taken place only along certain channels and to a much more limited extent than in the Colorado mine.

Calcite leaching is the only instance where marked impoverishment of any one constitutent occurs, except in copper-bearing

[8] Allgemeine und chemische Geologie. Wilhelm Hertz, Berlin (1879), 1, 48.

[9] Geike, Textbook on Geology. 4th ed. New York (1903), 471.

veins or in the case of leaching the sulphur constituent of sulphides, in which cases the usual conditions are encountered.

Enrichment of vein matter has resulted from the leaching out of barren material, from the solution and reprecipitation of valuable minerals, and from mechanical concentration of valuable minerals by water. The leaching of the calcite from a vein reduces the density of the vein, but does not carry with it any appreciable minerals of value. Therefore, the leached portion contains a much greater value per ton than the primary ore. This is very pronounced in the Colorado and Eastern mines, where it can be shown that this leaching alone has increased the value per ton about 100 per cent. The leaching of iron and manganese, while affecting the ore value to some extent, is relatively unimportant.

In all the veins some solution of gold has taken place. In copper-bearing veins and in manganese-quartz veins this has no doubt been an important factor, but the rapid erosion of the surface has washed away most of the leached material and has left exposed on the surface the enriched portion of the vein where precipitation has taken place. In veins of quartz, manganese, and calcite, the typical veins of the Philippines, the solution of gold appears to have been very slight and the leaching effect of manganese-bearing veins discussed by Emmons [10] appears to be lacking, but only observations in shallow workings are available. This condition will be discussed in a separate paper.

The highest values have been due to mechanical concentration of valuable minerals in crevices, streaks, and waterways within the vein or next to one of the walls. These are of common occurrence. In manganese-bearing veins soft streaks of black oxides of manganese are found, frequently extending from the surface to almost a hundred meters in depth, which carry exceptionally high values in gold. It is probable that part of this gold was precipitated from solution, but the greatest part seems to have resulted from mechanical concentration. In manganese-free veins rich streaks, carrying large amounts of iron oxide or iron and copper oxides, are common. The large volumes of water that flow through the veins during each rainy season must of necessity carry with them valuable particles which are filtered out at a lower depth as the fissure or waterway fills with sediment.

[10] *Bull. Am. Inst. Min. Eng. for 1910* (1910), No. 47, 767.

So far as development has gone at the present time, no secondary zone of secondary enrichment has been found in copper-free veins, which tends to strengthen the assumption that enrichment has been accomplished mechanically. In practically all cases the richest ore is found near the surface, and the values found so far appear to decrease with depth until the unaltered ore is reached.

The following table gives the principal gold-bearing veins in the Philippines with their chief characteristics.

TABLE I.—*Gold-bearing veins.*

SUYOC.

Mine.	Type of vein.	Width.	Strike.	Dip.	Vein filling.	Minerals.	Secondary enrichment.	Milling character.
		Meters.						
Elizabeth	Fissure	1	NE-SW		Quartz, calcite	Gold, copper, lead, zinc, iron, manganese.		
Quien Sabe	do	1 to 2	N-S		Quartz	Gold, pyrites, copper.		
Palidan	do	1 to 5			do	Gold, pyrites		

BAGUIO, BENGUET.

Mine.	Type of vein.	Width.	Strike.	Dip.	Vein filling.	Minerals.	Secondary enrichment.	Milling character.
Headwaters	Fissure in andesite.	2 to 8	N 65° E	50° N. W.	Quartz, calcite, manganese.	Gold, galena, pyrites, manganese.	In manganese streaks	Concentration in part, principally fine grinding and cyanidation.
Consolidated	do	10 to 30	S 70° E	65° S. W.	Crushed quartz	Gold, pyrites, manganese.	On foot and hanging walls and along manganese streaks.	Fine grinding and cyanidation.
Bua	Fissure in andesite (2 veins).	1.5 each	N 70° E	65° S. W.	Calcite, manganese.	do	In streaks of manganese.	Do.
Fianza	Fissure in andesite.	2 to 10	S 70° E	40° S. W.	Quartz	Gold, pyrites	Enriched portion has been eroded.	Concentration, fine grinding, and cyanidation.
Madison	Fissure in andesite and partly contact with diorite.	5 to 10	S 55° E	85° S. W.	Quartz, calcite, manganese.	Gold, pyrites, manganese.	Very marked in manganese streaks.	Fine grinding and cyanidation.
Camote - Clayton.	do	5 to 10	S 55° E	85° S. W.	do	do	do	Do.

Eileen	Fissure in andesite.	3	S 55° E	70° S. W.	do	do	In streaks of manganese	Cyanidation.
Lincoln Fraction.	Fissure in diorite.	5	S 55° E	45° S. W.	Calcite	Gold, pyrites		
Kelly No. 3	Fissure in andesite.	3 to 5	E and W	70° S.	Quartz	Gold, gold telluride, pyrites.	Along the walls	Concentration, followed by cyanidation.
Kelly South Slope.	do	4 to 7	S 80° E	65° N.	do	Gold, pyrites	General near surface	
Muyot	do	3 to 6	S 80° E	65° N.	do	Gold, pyrites, copper.	Occasional rich streaks, values are leached.	Concentration and cyanidation.
Tejon Dike	do	2 to 4	S 80° E		do	Gold, pyrites		
Emerald Creek	do	2 to 8	S 45° W	60° N. W.	do	Gold	In seams and pockets, vein much oxidized.	
Major Engineer.	Contact shale and andesite.	2 to 3	N 80° E	80° N.	do	Gold, pyrites		
Major	Contact sand, stone, and andesite.	3 to 6	N 60° E	60° N. W.	do	do		
Major Electrician.	Fissure in andesite.	3 to 5	N 25° E	57° N. W.	do	Gold		
Copper King	do	4 to 6	approximately E and W		do	Gold, pyrites, copper.		

AROROY, MASBATE.

Mine.	Type of vein.	Width.	Strike.	Dip.	Vein filling.	Minerals.	Secondary enrichment.	Milling character.
Colorado	Fissure in andesite, possibly contact.	5	N 45° W	70° N. E.	Quartz, manganese, calcite.	Gold, manganese	Very marked in manganese streaks and by leaching out of calcite.	Cyanidation.
Eastern Nancy No. 1.	Fissure in andesite.	3 to 10	N 45° W	70° S. W.	Calcite, quartz, manganese.	Gold, pyrites, manganese.	Very marked in upper workings and along manganese streaks.	Do.
Keystone	do	3 to 5	N 40° W		Quartz, calcite, manganese.	do		
Tengo	do	3 to 5			Brecciated quartz	Gold, pyrites	In upper workings	

PARACALE, AMBOS CAMARINES.

Mine.	Type of vein.	Width.	Strike.	Dip.	Vein filling.	Minerals.	Secondary enrichment.	Milling character.
San Mauricio	Fissure in schist and gneiss.	1 to 3	N 10° E	70° S. E.	Quartz	Gold, silver, copper, pyrites, galena.	Along foot wall	Concentration and smelting or roasting and cyanidation.
Tumbaga	Contact andesite and sedimentaries.	stringers	NE-SW		Calcite, quartz	Gold, lead, zinc, pyrites.		Free milling or concentration.
Longos Point	Fissure in gneiss.	10	NE-SW		Quartz	Gold, pyrites		
Navotas	do	stringers	NE-SW		do	Gold, lead, zinc		
Nalasvetan	Enriched zone in andesite.	5 to 10 (pockets)	N 30° W		Silicified material	Gold, manganese, pyrites.	Surface	Free milling near the surface.

NOS.   PROVINCES.

1. ILOCOS NORTE.
2. CAGAYAN.
3. ABRA. SUB. PROV. ILOCOS SUR.
4. ILOCOS SUR.
5. MOUNTAIN PROVINCE.
6. UNION.
7. NUEVA VIZCAYA.
8. ISABELA.
9. PANGASINAN.
10. TARLAC.
11. NUEVA ECIJA.
12. ZAMBALES.
13. PAMPANGA.
14. BULACAN.
15. TAYABAS.
16. BATAAN.
17. RIZAL.
18. CAVITE.
19. LA LAGUNA.
20. BATANGAS.
21. AMBOS CAMARINES.
22. ALBAY.
23. SORSOGON.
24. CAPIZ.
25. ANTIQUE.
26. ILOILO.
27. OCCIDENTAL.
28. ORIENTAL.
29. ZAMBOANGA DIST., MORO.
30. LANAO DIST., MORO.
31. MISAMIS.
32. AGUSAN.
33. SURIGAO.
34. COTABATO DIST., MORO.
35. DAVAO DIST., MORO.

LEGEND

Vein Gold Deposits

FIG. 2.—Showing localities where gold-bearing veins have been found.

Fig. 2 shows the localities in the Philippines where gold-bearing veins have been found.

VEIN GOLD DEPOSITS

SUYOC

The Suyoc mineral district, located in the Mountain Province, about 65 kilometers north of Baguio, contains a number of gold-bearing veins, varying from 1 to 4 meters in width. The vein-filling is mostly quartz, but occasionally stringers of calcite are found along the walls. Manganese is very subordinate, and was found in noticeable amounts in only one vein. Several veins carry tellurides, but in the majority of cases the gold was found free or associated with zinc, lead, copper, and pyrites.

The veins are found in conglomerate, diorite, andesite, andesite breccia, and along the contacts between igneous and sedimentary formations. The fissuring seems to have occurred after the formation of the sedimentaries, and was probably influenced by the intrusion of the Bagan granite, which lies west of the district.

BAGUIO DISTRICT

The Baguio district is located near Baguio, Benguet, and occupies an area of about 100 square kilometers. This district was profoundly shattered, and probably contains as many mineral veins as any district of its size in the world. Some of the veins are shown in Plate I. It can be divided according to the class of veins into four distinct sections:

1. The Antamok Valley: The characteristic vein matter is quartz, manganese, and, in a large number of cases, calcite. The gold occurs in the metallic state, but is also associated with iron pyrites, insignificant amounts of copper, and, in some cases, with galena and silver.

2. Itogon River: Calcite predominates in fissure veins in the diorite. A few quartz stringers were found carrying copper. Gold values are low.

3. Gold Creek: Calcite is almost entirely absent. Numerous quartz veins are found carrying free gold values and varying amounts of iron pyrites. Quartz veins carrying tellurides were found in the northern part of this group. Toward the south, copper values increase, and veins containing appreciable amounts of copper and lead are noticeable. Two veins carrying cinnabar were also discovered.

4. Bued River: A large percentage of copper is found in the majority of the veins, usually accompanied by high gold values. Calcite is absent.

Antamok Valley veins.—The characteristic veins of this section are represented by the Headwaters, Camote-Clayton, Gomok, and Eileen. These are made up of compact calcite, manganese, and varying amounts of quartz. In general the manganese bands representing secondary ore contain the highest values, but high assays are also obtained from the quartz and calcite. However, the last two are very irregular in the distribution of values, and are barren in many places.

No honeycomb quartz was found in this region. This circumstance, together with the regularity of the calcite content of the veins, leads to the conclusion that in certain instances the quartz was deposited in the fissure first, and that a second fissuring took place, after which the calcite was deposited. Veins are found containing quartz and manganese without any calcite, as in the Benguet Consolidated and the Madison; and of veins of calcite without manganese, as in the Capitalist. Veins are also found in this section without calcite or manganese, but they have not been developed, although some of them are worthy of exploitation. The most prominent are the Otek, Emma, and the Sunrise Fraction.

The gold is about 30 per cent free-milling (30-mesh), and is occasionally found as small specks or plates that can readily be seen in the ore; iron pyrite is abundant in the quartz veins, but is subordinate in the calcite-bearing veins. Several mines have been successfully operated in this section.

Itogon River.—In this section calcite veins predominate, although one large vein, the Lincoln Fraction, was found containing quartz and calcite. The main calcite veins are the Capitalist, Hamilton, Wheeler, and Jefferson. These veins carry small values in gold, and have never been properly prospected.

Gold Creek.—The principal veins are large, strong, quartz veins, striking nearly east and west. Among these are Kelly No. 3, Kelly South Slope, Muyot, Midas, Lorenzo Pao, and Tejon Dike. Several veins striking northeast and southwest are found on the Kelly, Mayon, and Ascension groups.

An irregular arrangement of veins occurs in the Kelly North Slope group. Here four veins are found having different strikes, which results in several intersections within the property (fig. 3), each vein cutting at least one other group. Another feature peculiar to this group is the occurrence of telluride ore in the veins, and the comparative absence of free gold.

In the Major group are a large number of veins striking northeast-southwest. Many of them are contact deposits be-

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tween sedimentary and igneous rock. The vein matter is chiefly clear, white quartz carrying free gold. One vein in Major Creek was found containing beautifully crystalline wire gold.
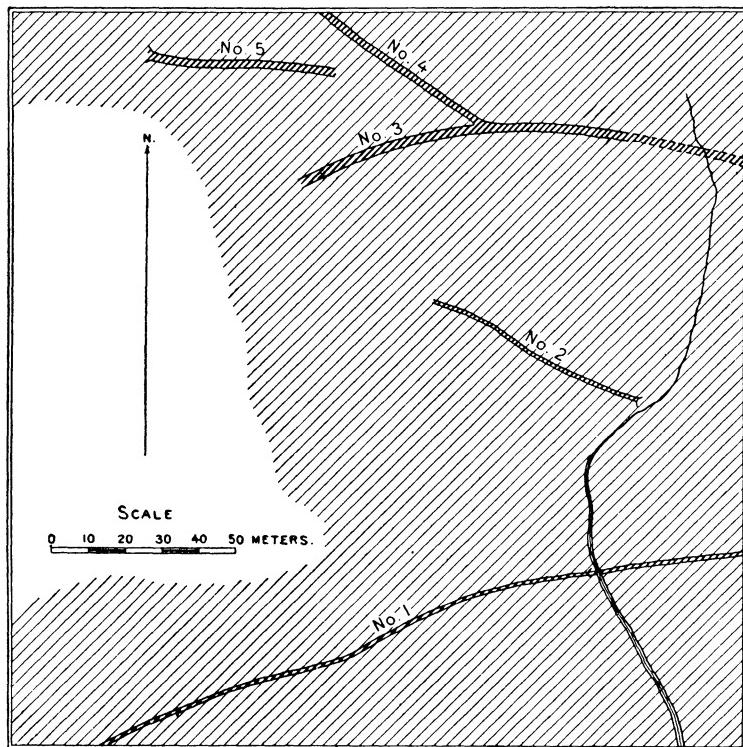
FIG. 3.—Veins on the Kelly group, north slope.

The east and west veins south of the Kelly group are very wide, and can be traced for several hundred meters on the surface. They are generally low in gold value, and carry varying amounts of iron pyrites and copper.

Bued River.—In this section the veins are characterized by high values in copper, sufficient in some cases to warrant their being classed as copper veins. In the zone of enrichment, gold values as high as 90 pesos (45 dollars United States currency) per ton have been found. The principal veins are the Copper King, Gray Horse, Union Jack, and Confederate. One vein carrying calcite and manganese was found in the Copper King group.

Evidence as already given points to the fact that two or more periods of fissuring had taken place; one period when quartz

and siliceous gold-bearing solution alone filled the fissures.   This was followed by a second fissuring, probably produced by the intrusion of the diorite, when calcite manganese gold-bearing solutions ascended in the Antamok Valley section.   This was later followed by the fracturing of the diorite, from cooling, and the deposition of calcite, free from manganese.   The copper, telluride, and lead veins probably were derived from local deposits, through which the ascending solutions passed, dissolving in their course the characteristic minerals.

PARACALE DISTRICT

The Paracale district is located in Ambos Camarines, Luzon, and occupies an area of about 200 square kilometers.   Some of the veins are shown in Plate II.   With the exceptions of the Tumbaga, Nalisvetan, and Navotas groups, the veins are compact quartz containing large amounts of iron pyrites with varying amounts of copper.   Among these are the San Antonio, Longos Point, and California, of Dinaanan Ridge, and the San Mauricio on May Cruz Mountain.   Most of these veins show visible gold in the oxidized zone.

The Navotas veins are narrow stringers of quartz with galena, sphalerite, iron pyrites, and gold.

The Nalisvetan deposit is a pockety, silicified mass of ore carrying free gold and some pyrites.

The Tumbaga deposit is a marked exception to the ores in the district.   It is a contact deposit, between shales and igneous rock.   The ore occurs as quartz and calcite stringers carrying galena, sphalerite, copper and iron pyrites, tellurides, and large amounts of visible wire gold.   It is very irregular and limited in extent.

AROROY DISTRICT

This district is located south of Aroroy, Masbate.   It comprises an area of about 80 square kilometers.   The principal veins are shown in Plate III.   Calcite, quartz, and manganese veins are characteristic of this district.   Of these the Colorado, Eastern, and Keystone are the most important.   It is evident that the quartz was deposited after the calcite, as shown in the leached ore where only a skeleton of quartz is left outlining the spaces formerly occupied by calcite crystals.

Colorado veins.—This deposit is found in igneous rock.   The hanging wall is andesite.   The footwall for a portion of the vein at least is decidedly different, and appears to be a separate intrusion.   In the places opened up, the ore is quartz (partly

honeycomb), manganese, and iron oxide. It presents a marked ribbon or banded appearance from the alternating layers of different classes of ore. This banding is generally parallel to the walls, but occasionally is seen in concentric rings. Numerous irregularities occur in the dip and strike of the vein, and horses are frequently encountered. The vein is from 3 to 6 meters wide, and can be traced for several hundred meters along the outcrop.

Eastern group.—There are several parallel veins in this group. The two principal ones are the Nancy No. 1 and the Nancy No. 2.

The Nancy No. 1 is a quartz-calcite-manganese vein from 4 to 6 meters wide. In the upper workings massive quartz predominates, but in depth practically the whole vein is calcite.

The Nancy No. 2 vein is in places only 3 meters from the Nancy No. 1. This distance varies greatly, owing to the variations in dip and strike in sections of the two veins. The vein is practically all calcite, although in places it contains a little quartz and manganese. It varies in width from 6 to 20 meters. It is low grade except along certain lines of enrichment 1 to 3 meters wide.

Keystone mine.—This property is located on Aroroy Mountain at the northern part of the district. The vein-filling is quartz (somewhat honeycomb), iron oxide, and small amounts of manganese. The quartz is much shattered, and is cut by numerous stringers of quartz deposited at a later period.

<div align="center">PLACER DEPOSITS</div>

The natural result of the weathering and erosion of a country containing numerous gold-bearing veins, as represented by Suyoc, Baguio, Lubang, Paracale, and Masbate, is the formation of placer deposits. Beside these localities, gold-bearing placers have been found in several regions where quartz prospecting has been carried on to a very limited extent and consequently comparatively few veins have been discovered, as in Nueva Ecija, Tayabas, Catanduanes, Mindoro, Mindanao, and other places. The localities from which placer gold has been reported are shown in fig. 4.

For the most part, placers are found in the valleys of the modern drainage system, but at least two cases have been discovered where the deposit was the result of ancient erosion. The best example of the latter class is the Cansuran deposit, Surigao, Mindanao.
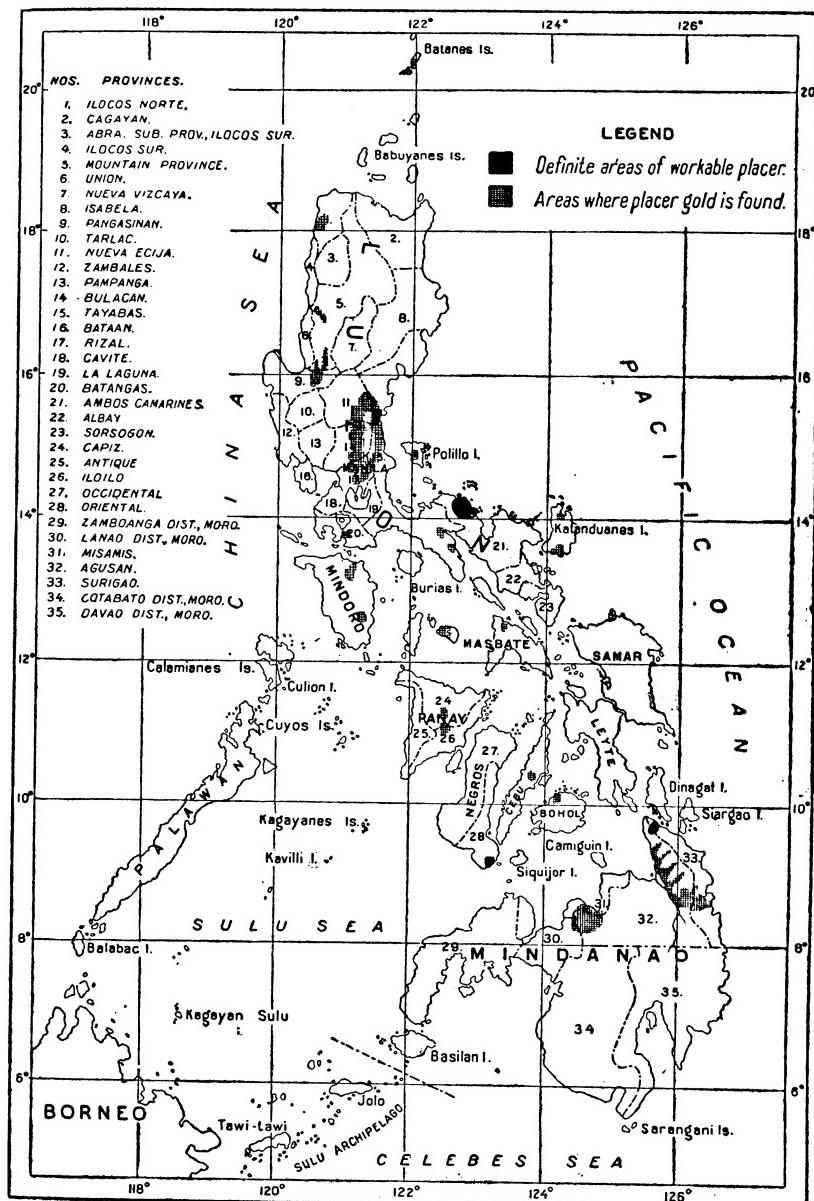
FIG. 4.—Showing localities from which placer gold has been reported.

Lepanto.—The placer deposit lies in the Comillas Valley of the Abra River which drains the Suyoc mineral district. The gold is derived from the erosion of the veins in the Suyoc mineral district. The amount of workable ground has been estimated

to be 27,000,000 cubic meters,[11] carrying about 50 centavos per cubic meter (20 cents United States currency per cubic yard).

Pangasinan placer.—The Agno and Tuboy Rivers that drain the Baguio and Lubang districts are very swift and carry the gold for great distances before it is deposited. The result has been the formation of an area of about 100 square kilometers of gold-bearing gravel in Pangasinan where the country changes abruptly from a precipitous mountain region to a large rolling plain. The rivers upon entering this plain have taken meandering courses, frequently changing their channels, and thus depositing the gold over a large fan-like area. They also very frequently overflow their banks, filling in large areas with flood gold. The gold deposited is fine and frequently in the form of rounded flakes. Coarser gold is found in the mountainous portion, where smaller streams flow into the Agno and Tuboy Rivers. Many such placers are worked by native miners. The gravel in Pangasinan is very deep except near the mountains, and contains many bowlders of all sizes wherever the river channel has been. This feature has made the testing of the ground a very difficult operation.

Nueva Ecija.—Gold from the Eastern Cordillera of Luzon has been distributed irregularly over a larger area than any other section of the Islands, forming hundreds of square kilometers of placer in Nueva Ecija, Bulacan, Rizal, and Tayabas. The most interesting feature is the occurrence of platinum in this placer. Some flat pieces have been found a centimeter in diameter. Grains weighing a milligram are of common occurrence. The two largest unbroken areas are found in Nueva Ecija, extending eastward from the line between Cabanatuan and Gapan and in Tayabas surrounding Dingalan Bay. The placer in Bulacan and Rizal is found principally along stream beds.

Ambos Camarines.—There are four sections in this district where placer gold is found: 1, Mambulao; 2, Gumaus; 3, Paracale River; and 4, Maliguit.

The Mambulao placer has not been thoroughly tested. Gold is found in the gravel surrounding the bay. It is derived from several large quartz veins in the San Mauricio and Robinson groups, and from stringers in the schist and gneiss.

The Gumaus placer is very different in character from the other deposits in the district. The gold is found in rounded grains of a clear yellow color. Very few crystals or flakes are found. A large number of rich stringers, many of which con-

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[11] Appendix, Report of the Philippine Commission (1908), 317.

tain galena and sphalerite, but no very important quartz veins, have been found in the immediately surrounding hills.   There is also a smaller percentage of black sand than in the other localities of this district.

The Paracale River placer lies in an elliptical basin covering an area of several hundred hectares.   The bed rock is granite gneiss, and the alluvium varies from 6 to 14 meters in depth. The concentrates caught on the tables of the dredge are made up of about 51 per cent magnetite, 16 per cent limonite, 21 per cent pyrite, and 12 per cent nonmetallic material.   The gold is mostly angular and crystalline; crystal trees and minute octohedrons are of common occurrence.   The larger grains of gold are usually attached to quartz grains.   This deposit has been described in detail by Fanning and Eddingfield.[12]

The Maliguit placer is found along various sections and branches of the Maliguit River.   It presents about the same general characteristics as the Paracale River placer.

Masbate.—The placer deposit lies in the valley of the Guinobatan River, Aroroy.   The gold is very fine and difficult to recover.   It was derived mostly from the numerous large veins of calcite quartz and manganese and from small quartz veins. It has been claimed that the presence of manganese in the veins prevents the formation of placer in accordance with Emmons' theory of the solution of gold.[13]   While this may apply to a limited extent, conditions are such as to justify hesitation in making its application general.

Mindanao.—Placer deposits are found at Placer, Cansuran, and Lubangan, Surigao; along several streams on the eastern side of the Agusan River, Butuan subprovince; and in the valley of the Pigtao River, Misamis.   Of these, the Cansuran deposit is of the greatest interest.   The gold is very coarse and is found in well-rounded grains.   Some pieces have been found weighing over 30 grams.   The alluvium is found on the crests and sides of the hills as well as in the valleys, and therefore represents an old deposit which has passed through some geological movements which raised it in part above its old bed.   This deposit has been described in greater detail by Eddingfield.[14]

[12] *This Journal, Sec. A* (1912), 7, 213.

[13] The agency of manganese in the superficial alteration and secondary enrichment of gold deposits in the United States. *Bull. Am. Inst. Min. Eng. for 1910* (1910), **No. 47**, 767.

[14] *Min. Resources P. I. for 1911, Bur. Sci., Div. Min.* (1912), 27.

Other districts.—Placer gold has been found in Ilocos Norte, Polillo, Batangas, Bondoc Peninsula in Tayabas, Mindoro, Catanduanes, Sibuyan, Panay, Cebu, Negros, and Bohol. Very little is known of these deposits. Some are known to be of very limited extent, while others, particularly in Mindoro, may prove to be very extensive. The localities where placer gold deposits have been reported are shown in fig. 4.

ILLUSTRATIONS

PLATE I

Mineral veins in the Baguio mineral district.

PLATE II

Mineral veins in the Paracale mineral district.

PLATE III

Relief map of Aroroy district.

TEXT FIGURES

FIG. 1. Showing faulting of the "Tejon dike" on the Ascension group.
2. Showing localities where gold-bearing veins have been found.
3. Veins on the Kelly North Slope.
4. Showing localities from which placer gold has been reported.

PLATE I. MINERAL VEINS IN THE BAGUIO MINERAL DISTRICT.

PLATE II. MINERAL VEINS IN THE PARACALE MINERAL DISTRICT.

PLATE III. RELIEF MAP OF AROROY DISTRICT.

A BONUS SYSTEM FOR THE PURCHASE OF PORTLAND CEMENT

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INTRODUCTION

In the first paper from this Bureau on the subject of Portland cement,[1] the efficiency of modern cement specifications and standard methods of testing were discussed. It was made evident that the ability of a cement to pass even the most approved specifications did not prove either its real or relative value in construction work, and that no tests had been devised which would give definite information about the behavior of cement both before and after induration. Since then information concerning the physical and chemical properties of Portland cement has increased, and standard specifications have shown a corresponding improvement; but they still leave much to be desired, and both the accuracy of standard methods of testing and the efficiency of standard specifications must undergo considerable change before they will secure the manufacture and purchase of Portland cement having the desired constancy in volume, strength, setting properties, and sand-carrying capacity.

The weakness of all cement specifications is due largely to the lack of definite knowledge concerning the chemical and physical properties of Portland cement. In fact, the results obtained from standard tests are so little understood that they do not enable us to arrange the various products in their true order of merit. Consequently:

(1) The chief object of testing is defeated, and it is necessary to specify minimum requirements which are intended only to cover the lowest limits which can be allowed on the work and to provide for lack of uniformity in tests as well as in real quality.

(2) There is practically no difference between the qualities and properties of a rejected and of an accepted cement in the immediate vicinity of the limit set by specifications; and it is often impossible to avoid the use of inferior material.   .

(3) As quality is specified, the enforcement of cement specifications usually makes it compulsory to award contracts to the

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[1] Reibling, W. C., and Salinger, L. A., *This Journal*, Sec. A (1908), **3**, 137–185.

lowest bidder regardless of the advisability of purchasing better material at a reasonably higher price.

(4) The awarding of contracts to the lowest bidder offers little incentive to produce a higher grade cement than that which will meet the specified minimum requirements. In fact, many manufacturers have to cut down their burning and grinding expenses to the lowest possible figure in order to secure sufficient sales.

The importance of always securing good cement is enhanced in the Philippines where most of the material comes a long distance by sea and where the cost of transportation is high; and many attempts have been made to establish a system of inspection and purchase which would insure the importation of nothing but satisfactory cement, and thus eliminate costly rehandling and troublesome delays which always accompany rejected cement, and which heretofore have spasmodically occurred to the detriment of all interests involved. At times, local officials have bought cement on reputation and personal experience, irrespective of cheaper brands then available. To our knowledge none of the cements so purchased were other than first-class. On the other hand, all cements which have given questionable or unsatisfactory results were purchased from the lowest bidder. Nevertheless, accusations of personal motives and prejudice, or the possibility of such, and the cry of unfair treatment from local agents of other brands ultimately forced officials to purchase on a basis of quantity rather than quality.

Similar attempts and results have been of common occurrence in other countries, so that the following brief history of the local operations of standard cement specifications, and, in fact, the entire discussion throughout this paper, are general in their application.

OPERATION OF STANDARD SPECIFICATIONS

Previous to the year 1907 the local standard for Portland cement was based upon the requirements of the 1902, U. S. Army specifications. During this time the engineer in charge of the construction of the water-supply system for Manila purchased a certain high-grade cement which had an excellent reputation and always passed well above the specifications in use. It was well burned, finely ground (about 88 per cent passed the standard 200-mesh sieve), its sand-carrying capacity was large, its packing was good, and different shipments received from time to time showed a remarkable uniformity in physical and chemical properties. However, certain manufacturers objected to the purchase of this cement on the ground that they were willing

to furnish cement for less money which would meet all of the
requirements of the specifications; and, finally, the engineer
was forced against his best judgment to use other and cheaper
material. The products then obtained often failed to pass, and
much of the cement barely passed, the specified requirements.
At times, workmen and inspectors complained about their setting
and hardening properties; and, at all times, their use was accom-
panied by considerable controversy, uncertainty, and confusion,
which involved considerable expense and vexatious delays.

In 1908 a special committee was appointed to improve these
conditions. They advised the adoption of specifications similar
to those of the American Society for Testing Materials, but
slightly modified so as to be practicable under tropical conditions.
These specifications went into effect in April, 1908, but they
failed to secure the desired improvement.

About this time another attempt was made to purchase cement
on a basis of quality. The purchasing agent inserted on his
bids the words "selection and award of this contract will be
made on a basis of the quality of the cement offered." This
brought forth the criticism that a personal equation of opinion
and prejudice had been introduced, which defeated the purpose
of the specifications; and the action of the purchasing agent
was not approved. In 1912, he again inserted the same clause,
and again merchants entered a vigorous protest. The matter
was referred to a special committee, which reported as follows:

After careful consideration, the committee fails to find any just cause for
criticizing the Purchasing Agent for inserting in his request for bids the
words "selection and award of this contract will be made on a basis of
quality of cement offered." However, as the specifications themselves fix
the minimum requirements, and as it is impossible to determine in advance
the quality of cement which may be delivered, we believe that this clause
should apply to the rejection of cements which have previously proven
unsatisfactory, or, to cements which have not yet established for themselves
a reputation for general reliability and soundness. Interpreted in this
manner, the clause above referred to is neither unusual nor unreasonable.

In support of this conclusion, the committee quoted from
paragraph 11, page 8, of the 1912 Government Specifications,
which reads as follows:

Bids for furnishing cement, or for doing work in which cement is to be
used, shall state the brand of cement proposed to be furnished and mill by
which made. The right is reserved to reject any cement which has not
established itself as high-grade Portland cement and has not been made by
the same mill for two years and given satisfaction in use for at least one
year under climatic and other conditions at least equal in severity to those
of the work proposed.

The presence of such a proviso fails to eliminate the possibility of a personal motive or prejudice in selection.   Furthermore, the rejection of all cements except those of established reputation would practically place the consumer at the mercy of present manufacturers.

On October 30, 1912, the cement specifications of the Government of the Philippine Islands were again changed by Executive Order No. 75, and now they conform to the 1912 specifications of the United States Government.   As there are no vital differences between the latter and the specifications of the American Society for Testing Materials, the change can not be regarded as beneficial.

During these six years, the quality of the cements received was equally as unsatisfactory.   The records of this Bureau show that:

(1) The best products received from different manufacturers varied considerably in character and efficiency.

(2) While in certain instances different shipments from the same mill showed a remarkable uniformity in quality, in others, we have met with sound and unsound, slow and quick-setting cements, and cements which developed both low and high 7-day tests, the value of which was no criterion of the ultimate strength.

(3) At times several shipments showed an apparent intentional decrease in efficiency.   New cement factories, especially, have been known to submit very good material at first, and then, as soon as their product had gained a suitable reputation, to cut down grinding and burning expenses and market an inferior product.

The differences between different brands of high-grade cement is readily accounted for.   I have inspected many large plants in Asia, Europe, and America, and have found adequate reason in local conditions for the peculiarities of many products which laboratory tests had revealed.   The quality of the best product from any mill depends more or less upon the nature of the raw materials used, the processes of manufacture employed, and the influences of various factors on the cost of production.   For instance, a uniform shipment, whether good or bad, was always associated with large storage bins for the ground cement.   On the other hand, the cement received from one factory, where the storage capacity was so limited that the cement was packed almost as soon as it left the grinder, usually showed considerable variation between successive samples taken from the same shipment.   It is evident that variations in the product of the grinders

and kilns become minimized when several hundred tons of cement become mixed in the same bin. The skill of the workmen, the kind of kilns and fuel used, the efficiency of grinders and mixers employed, as well as the hardness, purity, uniformity, and chemical composition of the raw materials are essential factors which vary more or less at different plants. However, a gradual falling off in quality is usually the result of deliberate intention. The manufacturer can control the quality of his product within reasonable limits; and, as he knows the character of his cement, no manufacturer unknowingly sends out whole shipments of poor material.

Manufacturers as a rule are anxious to supply satisfactory material, but they claim that the policy of purchasing from the lowest bidder compels them to direct their main efforts toward cutting down operating expenses rather than toward perfecting their cement. The manager at one plant made this point very clear. When asked if he did not think that better burning and finer grinding would improve his product, he replied: "Certainly, I could increase its efficiency about 20 per cent, and it would cost only about 8 cents per barrel to do so, but the Philippine Government will not pay to have it improved. Our cement passes the specifications as it is, and in order to get the contract we have to figure close to the quality specified. At first we bid only as low as good practice permitted, but, after losing several contracts because cement inferior to ours sold at a few centavos, or even one centavo, less, we had to change our policy." Our own extensive investigations on the physical and chemical properties of Portland cement made the truth of this statement very apparent. For best results, the raw materials must be carefully proportioned, finely ground, thoroughly mixed, and hard burned, and the finished product must be ground to extreme fineness. Therefore, efficiency is obtained only at a corresponding expense to the manufacturer, and the practice of awarding contracts to the lowest bidder has tended to limit the quality of the cement and discourage the best manufacturing practices. It also has failed to obtain the best results from the standpoint of relative cost and efficiency.

Some time ago the Philippine Division of the United States Army advertised for bids on 75,000 barrels of Portland cement to be used for fortification work at Corregidor. The three lowest bids were as follows:

(*a*) A Belgian cement at 4.36 pesos per barrel.

(*b*) An American cement at 4.38 pesos per barrel.

(*c*) An English cement at 4.38 pesos per barrel.

The maximum difference in the cost of the three cements was only 2 centavos a barrel, or 1,500 pesos on the contract for 327,000 pesos. A low estimate of the total cost of the concrete construction work is six times that of the cement, or 1,962,000 pesos. Fifteen hundred pesos represent only 0.076 per cent of the total cost of the concrete; yet, other conditions being equal, the difference of 1 per cent in the efficiency of the cement represents, in durability and in strength of the concrete, a value of 19,620 pesos. That there may be a difference in concrete efficiency of as much as 25 per cent even between two cements of the same brand, both of which pass the standard specifications, is illustrated in Table III. The actual difference in representative samples of two of the above cements is given in Tables I and II, in which the cements are designated as No. 1 and No. 2.

TABLE I.—*Results obtained by subjecting two cements to the tests of the specification of the American Society for Testing Materials.*

Test.	Results.	
	Sample No. 1.	Sample No. 2.
Specific gravity:		
Dried at 100 °C	3.14	3.08
Ignited	3.17	3.19
Composition:	*Per cent.*	*Per cent.*
Loss by ignition	1.03	2.94
Content of magnesia (MgO)	1.34	2.83
Content of sulphuric anhydride (SO_3)	1.16	1.19
Fineness:	*Per cent.*	*Per cent.*
Through the 200-mesh sieve	87.0	77.4
Through the 100-mesh sieve	97.8	95.2
Time of setting:	*Hours.*	*Hours.*
Initial set	2.1	1.6
Final set	4.3	3.6
Soundness in steam, air, and water	sound	sound
Tensile strength:	*Pounds per sq. inch.*	*Pounds per sq. inch.*
7-day, neat mortar	739	653
28-day, neat mortar	745	707
7-day, 1 : 3, Ottawa-sand mortar	310	313
28-day, 1 : 3, Ottawa-sand mortar	422	379

The figures in Table I prove that both cements passed all the requirements of the specifications. However, sample No. 1 is

better burned, finer ground, and contains less free lime than sample No. 2. Its great superiority to No. 2 is shown by Table II.

TABLE II.—*Tests which show the difference in efficiency betweeen cements, both of which passed all the requirements of standard specifications.*

	Sample No.	Strength in pounds per square inch.[a]				Relative efficiency, based on the strength of No. 2.	
		7 days.	28 days.	3 months.	2½ years.	3 months.	2 years.
Tensile strength of neat mortar ----------------	1	739	745	756	[b]716	105.3	110.0
Do -----------------	2	653	707	718	[c]651	100.0	100.0
Compressive strength of neat mortar-----------	1	4,080	6,030	8,800	11,450	116.6	115.8
Do -----------------	2	7,050	8,250	7,550	9,890	100.0	100.0
Tensile strength of 1:3, Ottawa-sand mortar--	1	310	422	429	418	117.9	150.0
Do -----------------	2	313	379	364	278	100.0	100.0
Compressive strength of 1:3, Ottawa-sand mortar-----------------	1	2,580	3,470	3,700	4,860	139.1	137.4
Do -----------------	2	2,080	2,565	2,660	3,537	100.0	100.0

[a] Each value represents the average of ten determinations.
[b] Total change in the length of a bar of neat cement No. 1 = 0.047 per cent expansion.
[c] Total change in the length of a bar of neat cement No. 2 = 0.098 per cent expansion.

The above does not represent an unusual or an abnormal experience. Some Portland cements which pass standard specifications are far inferior to sample No. 2 and some are superior to sample No. 1. In this case the superiority of sample No. 1 manifests itself in the specified tests, but very often the direct opposite is true, as the decrease in strength or the change in volume with age may be very great. In fact, some cements have given very satisfactory early results, and then, after several months, have disintegrated entirely.

Contracts awarded to the lowest bidder have not always secured the poorest cements. The location and operating conditions of some plants are so favorable that in certain markets they can undersell all other competitors without supplying inferior cement. For example, it is known that one manufacturer pays only 80 centavos per ton for limestone and 3.10 pesos for coal, while the same quantity of material costs another plant, which competes for the same markets, 1.70 pesos for limestone and 6.50 pesos for coal. Accordingly, in some localities, such as the Philippines, certain manufacturers can underbid other competitors and still supply a high-grade cement at a fair margin

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of profit; and, as a result, there are many local officials who believe that the present system for purchasing cement is the most economical and that any expenditure in excess of the lowest bid would be only an unnecessary expense. However, the records of cement testing show that the manufacturers who secure such contracts supply cement which tends to meet the minimum requirements of our specifications rather than those of a high-grade cement. This is especially true of cements imported into the Philippine Islands, where standard, 1:3, Ottawa-sand mortars, showing a strength over 400 pounds per square inch between the periods of three months and two years, are as rare as they should be common.

Careful investigation has shown that practically all of the cements which have been purchased by the local Government from the lowest bidder could have been considerably improved at a very small expense by better burning, by proper seasoning, or by finer grinding. The following instance will serve to show that the same is true of Portland cements purchased in other parts of the world. One of the best-known, high-grade, American cements was reground in a tube mill so that 88 instead of 78 per cent passed a 200-mesh sieve. Concrete made with this cement before and after regrinding was then molded into six-inch cubes and crushed after three months. In each case the sand, gravel, water, and the proportions by weight were the same. The average results obtained are recorded in Table III, which also includes the tensile and compressive strengths developed by the ordinary briquettes.

TABLE III.—*The strength developed by a high-grade Portland cement before and after regrinding.*

SIX-INCH, CONCRETE CUBES.

Cement.	Proportions by volume.	Age in days.		Compressive strength.			
		In moist air.	Weathered outside.	Total in pounds.		In pounds per square inch.	
				First crack.	Ultimate.	First crack.	Ultimate.
As received -------------	1 : 2 : 5	21	70	55,745	72,955	1,550	2,027
Reground --------------	1 : 2 : 5	21	70	64,408	92,135	1,800	3,559

ORDINARY BRIQUETTES OF 1:3, OTTAWA-SAND MORTARS SUBMERGED IN
FRESH WATER AFTER 24 HOURS IN MOIST AIR.

Cement.	Tensile strength in pounds per square inch.				Relative compressive strength in pounds per square inch.			
	7 days.	28 days.	3 months.	1 year.	7 days.	28 days.	3 months.	1 year.
As received _____	299	357	385	353	2,520	3,159	3,510	3,200
Reground _____	315	386	424	424	2,430	3,078	3,861	4,239

When reground, the cement gave 26.3 per cent higher concrete efficiency. It is estimated that the additional grinding would have cost the manufacturer less than 10 centavos per barrel. Computing on the basis of 5.24 pesos per barrel (the price named in the latest contract of the Bureau of Supply), this additional efficiency is obtained at an expense of less than 1.9 per cent of the cost of the cement. When we consider that the total cost of the concrete is about six times that of the cement, the extra expense for finer grinding becomes almost insignificant.

However, there are many who attach little importance to such facts. Portland cement is used in a rather crude manner and much of it where great strength is not of practical importance. This, and the somewhat general belief that a cement which meets the requirements of our specifications is good enough for all ordinary purposes, has induced many to belittle the importance of obtaining a more uniform and efficient product. Also, many claim that it would be useless to use better cement with poor aggregates such as are usually the only ones available for local construction work. This attitude is founded on a basis which is neither economical nor progressive.

If weak concrete meets the requirements, then cheaper material such as "adobe" stone, hydraulic lime, or natural cement should be used. On the other hand, for important permanent structures, the greatest economy and efficiency result from the intelligent use of the best cement obtainable at a reasonable cost. This is especially true in the Philippines where most of our sewers, retaining walls, bridges, buildings, etc., are frequently subjected to severe destructive influences such as typhoons, earthquakes, and floods. Structures must be built to withstand extraordinary rather than ordinary demands upon their strength

and durability, and the very best cement has proved none too good. The fact that the available aggregates are poor in quality or that cement is used in a crude manner serves only to increase the responsibility upon the cement; and, although a second-grade cement may be good enough for some purposes, usually a longer and a more satisfactory service will more than compensate for the greater initial expense of securing better material. Furthermore, if we purchase mediocre cement, and thus promote its manufacture, we can not hope to obtain uniformity in quality, without which the architect and builder are unable to figure on close margins. Structures are small now as compared to those which are likely to be erected in the future, but, even at the present time, the lack of certainty of securing cement which will retain a definite strength and not change in volume sufficiently to develop dangerous internal stresses is a source of great expense.

The most commendable feature of the present method of purchasing cement is the promotion of competition, which is a leading factor in keeping down market prices, and eliminating the possibility of personal motive or prejudice. Competition for our contracts has been fairly keen, but it has not been a competition which has induced the best manufacturing practices, supplied a uniformly high-grade product, or prevented the necessity of expensive rejections. In short, it has been a competition involving price rather than quality; and, unfortunately, it is impossible to correct the faults of a poor cement by increasing the amount used.

REQUIREMENTS FOR IMPROVED EFFICIENCY

Desirable results can be obtained only by establishing a reasonable standard for the purchase and use of the Portland cement which will be fair to the manufacturer and take into consideration the work capable of being done as well as the quantity of cement used. At the same time, the significance of inducing and fostering competition should not be overlooked because we must depend largely upon a condition of vigorous competition to keep the cost within reasonable limits.[2]

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[2] In 1909, I officially reported an instance where a cement manufacturer shipped his best product hundreds of miles by sea and then sold it for less than 4.50 pesos per barrel, while the community where the factory was located often paid from 7 to 9 pesos for inferior material. This practice was made possible by a heavy duty on all imported cements which enabled the only home factory to eliminate competition.

How, then, can manufacturers be induced to compete on a basis which demands the best product at a reasonably profitable price?

The most noteworthy attempt to solve this problem was instituted by the New York Rapid Transit Company when it contracted for cement manufactured according to certain stipulations. An expert was stationed at the mill at all times to inspect the process of manufacture, to reject any inferior material, to insist upon proper burning, grinding, and seasoning, and to test the cement before it was shipped.[3] Such an inspection at the place of manufacture can be conducted to the advantage of the manufacturer and the consumer, but it is only practicable when the contract involved calls for the purchase of a very large quantity of material. Many cement manufacturers are willing to coöperate with such a plan provided the inspector is a person of good judgment and experience. On the other hand, the purchaser would need to have extreme confidence in the inspector's honesty and ability. The difficulty of finding cement experts who would be acceptable to both parties is sufficient to prevent the general application of this system.

A practicable method would be to buy cement which will pass the minimum requirements of a standard specification as heretofore, and in addition offer for superior quality a bonus which will be a benefit to both manufacturer and consumer and induce nothing but the best manufacturing practices. Such a bonus system would promote a greater and a more desirable competition than the present system, because the manufacturers could furnish their best products at a lower price than heretofore and enter into fair competition with inferior cements from which little or no additional revenue could be expected.

None of the numerous attempts to establish such a system have proved satisfactory. Years ago it was the common practice to offer a bonus for cements which would give exceedingly high 7-day tests, but this practice was abandoned as soon as it became generally known that the quick-hardening, rotary cements usually develop such an abnormal decrease in strength that the slower

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[3] *Cement Age* (1905), 1, 75.

In this instance the manufacturer complied with the suggestions offered by the chief inspector, and tests carried on for five years showed a remarkable regularity in the accepted product. There also was a continued improvement in the quality of the cement which corroborated the original assumption that "an early stage, low pulling cement, which undoubtedly will show best results in the long run can be made in rotary kilns notwithstanding the general tendency of such commercial products to show abnormally high early results with a consequent retrograde movement later on."

hardening, set-kiln products often gave better results in time. Recently engineers have begun to realize that ordinary cement contains only about two-thirds of its weight of actual cement, and that the remainder is about as inert as ordinary sand because it has not been sufficiently pulverized, and there has been a growing tendency to award a bonus for extreme fineness.[4]   This is a step in the right direction, but many comprehensive tests show that the strength developed by different cements does not depend upon the degree of fineness.

Other conditions being the same, the degree of fineness affects the quantity of active material in a given bulk rather than the quality; and as an underburned Portland cement is easier to pulverize than a hard-burned product, the manufacturer can supply a more finely ground cement without a corresponding increase in strength.   The strength developed and maintained by Portland cement is the net result of many factors including, besides fineness, the influences of chemical composition, burning, and seasoning.

The present state of our knowledge does not enable us to specify either the conditions of manufacture or the properties of a cement having the greatest possible value; and, even if otherwise, manufacturing conditions, the nature of the available raw materials, and the bulkiness of the product are such that it would be impracticable to demand an ideal product.   On the other hand, our present knowledge is sufficient to enable us to specify and identify the characteristics of Portland cements which give the greatest efficiency which modern improvements for burning and grinding have made practicable, to promote and support the best manufacturing practices, and, accordingly, to secure Portland cement having the greatest uniformity and efficiency consistent with the principles of true economy.

The efficiency of Portland cement depends primarily upon the thorough sintering or fusing of the raw materials, and for best results it is very essential to burn at a high temperature and eliminate free lime.   The strongest cements require the highest burning temperatures because the formation of the high-calcium silicates and the low-calcium aluminates requires greater heat than is necessary to form the much weaker low-limed silicates and high-limed aluminates.[5]   The effects of the different

[4] *Eng. News* (1909), **62**, 105, 179, 230, 358.
[5] Schott, *Cement & Eng. News* (1910), **22**, Nos. 9 to 12.

kinds of free lime were thoroughly pointed out in previous papers from this laboratory.[6]

It is sufficient to state here that free lime tends to cause dangerous changes in the setting and hardening properties of Portland cement, and that the endurance of the early strength, the increase in strength with age, and the constancy in volume will be the greater the less free lime (or magnesia) the indurated cement contains.   Therefore, we can not hope to secure the desired efficiency and uniformity in quality unless the quantity of free lime is reduced to a very low figure.   The best burning and proper seasoning and storing produce a sound product which has a high specific gravity and a low loss by ignition; and, while it is impossible to obtain Portland cement which contains no free lime, the manufacturer should burn his materials so that no seasoning is required to produce a perfectly sound cement.

It is essential to increase rather than decrease the severity of the requirements for constancy of volume.

While the large use of concrete demonstrates beyond question its value as structural material, there are too many concrete structures now showing signs of incipient failure to permit us to relax in any way the demands of the standard specifications or our efforts to secure improvement in the quality of the cement.   If the use of Portland-cement concrete is to continue to increase, or even remain as great as at present, the engineer must be assured of its durability.   It is unfortunate, perhaps, that the present low prices of cement offer little inducement to the manufacturer to spend more money to improve quality, or to assume the additional cost involved in the storage of the clinker and the finer grinding demanded by Mr. Force.   It is an old axiom "that we get only what we pay for," and if the engineer is going to insist, as it seems proper he should, on the furnishing by the manufacturer, for important structures, of a cement which will pass the autoclave test, he should be prepared to offer an advanced price for such a cement.

It is universally recognized that neat Portland cement is not durable, and it is for this reason, and not from motives of economy only, that cement is used mixed with sand or other aggregates.   Until the cement manufacturers can produce a cement which will be durable when used neat, they should not relax their efforts toward the improvement of their product, and the engineer should not hesitate to adopt, and to insist that the cement shall pass, any test, no matter how severe, that will develop any latent unsoundness or tendency to expand in time after the concrete made from it has been hardened on the work.   Even though one must pay more for a cement that will meet such special tests than for one that will meet only those required

[6] Reibling, W. C. and Reyes, F. D., The chemical and physical properties of Portland cement: Parts I and II, *This Journal, Sec. A* (1910), 5, 367–418.

Part III, *ibid.* (1911), 6, 207–252.

Parts IV and V, *ibid.* (1912), 7, 135–195.

Abstract and summary, 8th Int. Cong. Applied Chemistry, III c. (1912), 5, 91–116.

by the standard specifications, the increased cost of the work as a whole will be small, and can be well afforded if it is an insurance against failure or renders it less likely.[7]

As already stated, the degree of final pulverization is another important consideration. The particles of Portland cement which are too coarse to pass a 150-mesh sieve may be considered as inactive clinkers, the finer grinding of which produces a cement whose efficiency depends upon the same conditions of composition, burning, seasoning, etc., as that of the impalpable power obtained from large clinkers. The only other consideration which the subject of fineness introduces is concerned with the permanency of the strength developed by the finest and most active particles. The durable nature of the indurated impalpable powder has been proved, and, considering that free lime hydrates more readily the finer its state of subdivision, the great benefits derived from fine commercial grinding are apparent.

The ultimate chemical composition may vary within wide limits, and Portland cements of the desired quality can be obtained from most of the mixtures now used. Nevertheless, a careful study of the available raw materials will show in each instance that some combinations are capable of giving better results than others, and usually one combination the best of all. Therefore, each manufacturer should be induced to study his raw materials until the most efficient mixture has been ascertained. Also, he must carefully regulate the raw mixture at all times. Otherwise it will be impossible to obtain a uniform product.

For best results the raw materials must be carefully selected and regulated, finely ground, very thoroughly mixed and hard burned, and the finished product must be of extreme fineness and properly packed. All of these factors are so important that we can not afford to neglect any one of them.

I do not believe that it would be advisable to formulate a bonus system on the present requirements of the American specifications as a standard. The clauses which permit a determination of the specific gravity after the sample has been ignited at a low red heat, a loss by ignition of 4 per cent, unsoundness in accelerated tests, and a 25 per cent residue on a 200-mesh sieve make it possible for rather poor grinding and burning to fulfill these requirements. A much more efficient standard is outlined

[7] Spadman, Henry S., The need of a more severe soundness test for cement, *Eng. News* (1912), **68**, 80.

in the recommendations for improving the present specifications which were given in a previous paper.[8]

<div align="center">PROPOSED BONUS SYSTEM</div>

In view of the foregoing, I suggest that Portland cement be purchased as heretofore from the lowest bidder who guarantees to fulfill the requirement of specifications, and that the following provisions be made for bonuses to be awarded for superior quality:

1. No bonus will be awarded unless the cement passes *all* of the specified requirements including perfect soundness after the steaming test and unless the cement is reasonably uniform in quality and suitably packed.

2. A bonus of 10 centavos per barrel will be awarded if the specific gravity is consistently above 3.10 (or the loss by ignition not greater than 2 per cent).

3. A bonus of 10 centavos per barrel will be awarded if the residue on the number 200 sieve is less than 15 per cent, and that on the number 100 sieve less than 3 per cent.

4. Provided the gravity is not less than 3.10 (or the loss by ignition not greater than 2 per cent), a bonus of 10 centavos per barrel will be awarded if the 28-day, 1: 3, standard Ottawa-sand briquettes show consistently an average tensile strength above 400 pounds per square inch.[9]

The above would provide bonuses for superior mixing, grinding, and burning, and would permit the manufacturer to earn 30 centavos (15 cents United States currency) per barrel in excess of the selling price. In Manila, 30 centavos is about 5.7 per cent of the usual cost of Portland cement and less than 1 per cent of the cost of concrete. On the other hand, such a system properly enforced ought to secure at least 10 per cent better concrete, eliminate the necessity of rejecting cement, and secure greater certainty in its use.

Owing to the varying influences of local conditions in different localities on the cost of manufacture, the values given in this proposed system are not arbitrary. However, the principles constitute the essential features, and they must remain fixed.

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[8] *This Journal, Sec. A* (1912), **7**, 189–191; also, *Met. & Chem. Eng.* Special number (Sept., 1912), **10**, 612; *Eng. News* (1913), **69**, 298, and *Cem. & Eng. News* (1913), **25**, 91.

[9] The above recommendations provide for the possibility of a well-burned cement with a lower specific gravity than 3.10, if the low gravity is not due to an absorption of volatile constituent, but our experience does not include such a possibility.

Good packing is insisted upon in order to prevent properly stored cement from serious deterioration. Perfect soundness (no warping, checking, cracking, or disintegrating after the hot test) is also essential, and it might be advisable, as recommended by H. J. Farce,[10] even to substitute the more severe autoclave test for steaming or boiling under ordinary pressure.

It is useless to insist upon soundness unless we also take into consideration the specific gravity (or the loss by ignition). We can season an underburned cement, or a cement made from poorly mixed or coarsely ground raw materials, until it passes the accelerated tests for soundness; not, however, without a corresponding reduction in the specific gravity and increase in the loss by ignition. Likewise, we can not rely upon the specific gravity or loss by ignition without taking into consideration the soundness. A nonseasoned Portland cement usually has a high specific gravity regardless of whether it is underburned or hard burned and regardless of the amount of free lime present. Therefore, a bonus is provided for perfect soundness in conjunction with a high specific gravity (or a low loss by ignition) for the purpose of securing a well-burned product.

Another bonus is provided for superiority in strength in order to induce a careful selection and regulation of the raw materials. Ordinarily it would not be advisable to base a bonus on the strength developed in twenty-eight days. If a cement contains more than a very small quantity of hard-burned free lime, then no reliance can be placed on the results of the early tests for strength. However, well-burned cements show little or no decrease in strength with age; and, since it is specified that no bonus will be awarded unless the cement is well burned; that is, unless it has a high gravity (or low volatile constituents) and is perfectly sound, no bonus would be granted except for superior permanent strength.

In conclusion, it may be stated that certain manufacturers, to whom the proposed bonus system has been submitted, have expressed their willingness to coöperate on such a basis. The agent of one company has written as follows:

The advantages to be secured from such a system as suggested are of so pronounced a nature to both the purchaser and to the contractor that it is not necessary to enlarge on them. The manufacturers would have every inducement to produce cement above the minimum requirements set by the specifications, and the bonus would undoubtedly cover the extra cost incurred for special care in packing, burning, and grinding. In the majority

[10] *Eng. News* (1911), **67**, 1111.

of cases, the manufacturer and his agent are very desirous to execute their contracts to the satisfaction of all parties, and *where financial conditions permit,* would prefer to supply material above the specifications in order to avoid any risk of loss through rejection and consequent dissatisfaction. The above expression of opinion has behind it the result of ten years' trading in cement and business here amounting to over 100,000 barrels since the beginning of the year. We shall be glad if it is possible to handle cement for the Government on the bonus system mentioned above, and shall be pleased to let you have any information from the factory that may assist in the furthering of this system.

SUMMARY

1. A résumé of the operation of standard specification for Portland cement shows the need of improving our contracting methods for the purchase of this material.

2. At present there is little incentive to induce the manufacturer to grind and burn to the degree of perfection that modern improvements have made practicable.

3. In order to secure the desired constancy in volume, strength, setting properties, and sand-carrying capacity, the raw materials must be carefully selected and regulated, finely ground, very thoroughly mixed, and hard burned, and the finished product must be of extreme fineness and properly packed. None of these factors can be neglected.

4. Increased efficiency can be obtained only at a correspondingly greater expense to the manufacturer, and Portland cement should be purchased on a basis of quality as well as quantity.

5. Desirable results can be obtained only by establishing a reasonable standard for the purchase and use of Portland cement which will be fair to the manufacturer and take into consideration the work capable of being done, as well as the quantity of cement used.

6. This standard must be applicable to a system which will induce and foster competition.

7. In view of the foregoing, it is suggested that Portland cement be purchased as heretofore from the lowest bidder who guarantees to fulfill the requirements of an improved specification, and that, in addition, bonuses be awarded for superior quality.

8. A bonus system is described, the enforcement of which, it is believed, would secure the desired results.

9. The bonuses specified permit the manufacturer to earn 30 centavos (15 cents United States currency) per barrel in excess of the selling price provided he supplies a well-burned, finely ground product and the standard, 1: 3, Ottawa-sand mortars

show consistently an average reliable strength of over 400 pounds per square inch.

10. In Manila the total bonus would average about 1 per cent of the cost of concrete. It would secure at least 10 per cent greater concrete efficiency, and practically eliminate the necessity of rejecting cements.

11. Cement manufacturers have expressed their willingness to coöperate on such a basis.

ALTERATION AND ENRICHMENT IN CALCITE-QUARTZ-MANGANESE GOLD DEPOSITS IN THE PHILIPPINE ISLANDS

By F. T. EDDINGFIELD

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The agency of manganese in the production of secondary alteration has been discussed by W. H. Emmons.[1] He states:[2]

Since there are no data which show the effect of highly carbonated waters on these reactions, I have so far as possible eliminated examples of gold deposits in limestone, and the discussion is confined mainly to deposits in noncalcareous rock.

From this statement and particularly from the discussion which follows, it appears that the case, where the ore deposit itself contains calcite, had not been separately considered. It is my belief that the majority of cases of manganiferous gold deposits which do not conform to the theories of secondary enrichment advanced by Emmons are calcite-bearing veins. *An examination of the descriptions of the ore deposits in the last section of the article mentioned above will show that the majority of deposits which do not show impoverishment in the upper level nor enrichment near ground-water level, are calcite-bearing. These cases will be cited later.*

Many ore deposits of the Philippine Islands are made up of quartz and manganese with large amounts of calcite. Veins of this character are so numerous that they may be said to represent an important type of Philippine deposits. Attempts have been made to apply Emmons' hypothesis to these ores; but investigations in the laboratory and in the field seem to indicate that the reactions which take place in this class of deposits are of such a character as to produce entirely different results.

These ores contain practically no copper. While I believe that, if the copper content is relatively small compared with

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[1] *Bull. Am. Inst. Min. Eng. for 1910* (1910), No. 47, 767.
[2] *Loc. cit.*, 772.

the calcite content, the results would be the same, I have not considered copper reactions in this discussion.

The principal characteristics of this class of deposits due apparently to the presence of the calcite are: 1, The mine waters are neutral.or alkaline at practically all horizons above groundwater level; 2, owing to this fact no free chlorine can be formed; 3, should nascent chlorine be formed, it would readily attack the moist calcite, so that little or no chlorine would remain uncombined and free to attack the gold; 4, should gold chloride be formed, some of the gold at least would be precipitated at approximately the same horizon by ferrous sulphate produced by the oxidation of the iron pyrites.

In the Philippine calcite-bearing ore deposits the manganese seems to be associated with the calcite in the primary ore.[3] All the evidence available confirms this conclusion. Therefore, wherever manganese is found, either calcite or calcium carbonate in solution is present and would neutralize any acids, or has been present and has already neutralized the acids. If any acids are formed, it is evident that where they are formed there is no calcite or calcium carbonate in solution and consequently no manganese. Under such conditions, ferrous sulphate would be formed, and it would appear that if there is insufficient calcium carbonate to neutralize the acid there would also be insufficient manganese oxide to oxidize the ferrous sulphate. This condition would leave active an agent which precipitates gold.

ANALYSES OF MINE WATERS

In the analyses of mine waters [4] it is noted that acid hydrogen was determined or found to be present in only 10 out of 29 cases. The facts that in the general average of mine waters 295 parts per million are calcium and 77 parts per million are the carbonic-acid radicle might account for some of the 19 cases where acid hydrogen was not reported and in which the mine waters were neutral.

Analyses were made of mine waters of the calcite-gold deposits of the Philippines to determine, primarily, free chlorine and acidity.

[3] Fanning, *Min. Resources P. I. for 1911, Bur. Sci., Div. Min.* (1912), 44.
[4] Emmons, *opus. cit.*, 773.

TABLE I.—*Mine-water analyses.*[a]

[Parts per million.]

Constituent.	No. 1.[b]	No. 2.[c]	No. 3.[d]
Chlorine (Cl_2) (free)	nil	nil	nil
Chlorine (Cl) (combined)	slight trace	slight trace	16. 8
Sulphuric-acid radicle (SO_4)	255. 9	283. 4	trace
Bicarbonic-acid radicle (HCO_3)	136. 6	190. 9	----------------
Carbonic dioxide (CO_2) (combined)	------------------	------------------	13. 2
Carbonic dioxide (CO_2) (free)	------------------	------------------	12. 0
Iron and aluminum oxides (Fe_2O_3, Al_2O_3)	1. 2	0. 8	----------------
Iron (Fe)	------------------	------------------	2. 2
Manganese (Mn)	slight trace	nil	nil
Calcium (Ca)	136. 5	123. 3	2. 8
Sodium (Na) not determined.			
Magnesium (Mg)	9. 3	17. 5	----------------
Free CO_2	1. 6 cc. per liter	5. 0 cc. per liter	----------------

[a] All analyses by V. Q. Gana, Bureau of Science.

[b] No. 1. Headquarters mine, Baguio. Upper workings 20 meters from the surface. Solution neutral to litmus.

[c] No. 2. Headwaters mine, Baguio. Forty meters from the surface. Solution neutral to litmus.

[d] No. 3. Colorado mine, Masbate. Solution reaction alkaline.

The ore above the point where the first two samples of water were taken is calcite and quartz carrying manganese in large amounts, about 1 per cent iron pyrites, and in places some galena.

In the analyses of these samples the large amounts of calcium, sulphuric-acid radicle, and bicarbonic-acid radicle, the small amounts of iron and manganese, and the absence of free chlorine are noteworthy features.

The Colorado water sample was obtained where the leached ore had had most of the calcite removed by surface waters and the sulphides had been mostly oxidized. This analysis is characterized by the alkaline reaction, the large amount of combined chlorine, combined carbon dioxide, and relatively high iron, as well as by the absence of free chlorine. In all three samples there is no agent present which could dissolve gold.

LABORATORY EXPERIMENTS

A mixture was made of finely ground material representing as nearly as possible the active constituents of the ore bodies. This

consisted of 45 parts calcite, 45 parts manganese dioxide, 5 parts ferrous sulphate, and 5 parts ferric sulphate.

Experiment No. 1.—Samples of this mixture were placed in vessels with filter bottoms. Through these a solution, consisting of about 10 per cent by weight of sulphuric acid and 10 per cent sodium chloride in 80 per cent water, was allowed to leach continuously, and the following analyses show the composition of the filtrate after given periods of time.

TABLE II.—*Analyses of water showing composition after given periods.*

Constituent.	Per cent.[a]	Per cent.[b]	Per cent.[c]
Chlorine (free)	nil	nil	nil
Chlorine (Cl) (combined)	1.55	1.89	1.3
Sulphuric-acid radicle (SO₄)	0.4	0.733	4.27
Carbon dioxide (CO₂) (combined)	0.0004	0.0004	nil
Carbon dioxide (CO₂) (free)	nil	nil	nil
Iron (Fe)	little	0.034	0.24
Manganese (Mn)	nil	0.124	little
Calcium (Ca)	0.13	0.067	0.105
Sodium (Na)	0.92	1.18	0.95

[a] Solution neutral to litmus after 48 hours.
[b] Became neutral to litmus after 72 hours. An iron salt precipitated immediately after passing the filter bed. Solution slightly acid.
[c] Solution acid after 75 hours.

After seventy-five hours the filtrate became decidedly acid and contained a large amount of ferric chloride. At this stage it was evident that the leaching solutions had formed channels in the ore and were reacting only upon the walls of the channels.

The results of Table II indicate that no free chlorine would be formed in a vein so long as the oxidizing waters were neutral, alkaline, or only slightly acid, and that free chlorine is formed only when the solutions are decidedly acid and iron is absent. When iron is present, ferric chloride is formed which acts as a solvent of gold in the presence of manganese dioxide. Experiments 14, 15, 16, and 17 in Emmons' paper[5] show that gold is dissolved when hydrochloric acid and manganese dioxide or ferric chloride and manganese dioxide are present.

Experiment No. 2.—A sample of the ore mixture was placed in a bottle with 0.5 gram of finely divided gold, 50 cubic centimeters of saturated sodium-chloride solution, and 400 cubic centimeters of 10 per cent sulphuric acid and agitated for eight

[5] *Opus cit.,* 782.

hours. No free chlorine was found in the solution, and no gold was dissolved.

Experiment No. 3.—A sample of the ore mixture was placed in a bottle, with 0.5 gram of finely divided gold and freshly made chlorine water, and agitated for eight hours. The resulting solution gave a strong test for free chlorine, but contained only a trace of gold.

Experiment No. 4.—Two parallel chlorination tests were run. No. 1 was made up of finely ground calcium carbonate, 0.5 gram of finely divided gold, and freshly made chlorine water. No. 2 was made up of finely ground quartz, 0.5 gram of finely divided gold, and freshly made chlorine solution. These were agitated for one hour. No. 1 solution gave a strong test for chlorine and calcium, and showed a trace of gold. The calcium was dissolved to form $CaOCl_2$ and possibly $CaCl_2$. No. 2 gave a strong test for chlorine, and showed a large percentage of gold dissolved.

In the case of No. 1 the chlorine attacked the calcium carbonate first, but the great excess of chlorine gave it an opportunity to dissolve some gold as well. Another test, in which the chlorine was in contact with the gold and calcite for forty-eight hours, showed that a very large percentage of the gold had been dissolved. The reaction of chlorine with calcite would be more important in an ore deposit where there is relatively so small an amount of chlorine.

Experiment No. 5.—Calcium carbonate was added to gold-chloride solution, boiled for five minutes, and filtered. No gold was precipitated.[6] The filtrate was almost colorless. It contained a large amount of calcium, probably as a complex salt of calcium and gold.

These experiments demonstrate that no acid could be formed in veins containing calcite, except in waterways in the parts of the vein where calcium carbonate is not encountered. It is probable that even in such cases the acid would travel but a short distance before coming in contact with, and being neutralized by, calcite or calcium carbonate in solution. Chlorine cannot be liberated except in the presence of acid, and consequently no free chlorine or very small amounts only would be formed in the type of vein under discussion.

If the gold were ever dissolved as gold chloride, it could be precipitated by ferrous sulphate, metallic sulphides, calcite, organic material, or bacilli at or near the same horizon.

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[6] W. H. Emmons recently has found that gold is precipitated from cold dilute solutions by calcite. I have not yet seen this in a publication.

Philippine calcite ores.—The ore deposits of this type in the Philippines are found in the Headwaters, Camote-Clayton, and Bua mines of the Benguet mineral district; and in the Colorado and Eastern mines of Aroroy mineral district, Masbate.

The Headwaters deposit is a fissure vein in the andesite made up of bands of calcite, quartz, and manganese oxide carrying about 1 per cent iron pyrites and traces of lead and copper. The calcite in places is about 6 meters wide, while in others it is very narrow and entirely disappears near the outcrop and in the vein where leaching has been extremely active. The manganese oxides are found in bands varying from 0.3 to 1.5 meters in width; these bands are irregular, and vary from 2 to 6 meters in width. The quartz is much fractured, and its sulphide contents have been mostly oxidized in the upper levels. The calcite in depth is compact and generally retains its sulphides unaltered, but near the surface it is fractured, channeled, and contains numerous stringers of manganese. The highest values are found in the manganese bands. With depth the manganese oxide seems to decrease and the calcite to increase. At and near the outcrop, high values are found. These seem to decrease more or less uniformly with depth.

The Camote-Clayton deposit is at least in part a fissure in andesite, but appears to follow the contact between andesite and diorite for a short distance. The gangue is calcite and quartz with large amounts of manganese oxides and some iron pyrites. In the upper workings the calcite bands are small; quartz bands are also subordinate. The main portion of the vein is manganese oxides (wad) including fragments of quartz and pockets of crystallized quartz, which are said to contain high values. The manganese bands vary in width from 4 to 12 meters. The calcite increases and the manganese decreases with depth. The gold values which are highest near the outcrop decrease with depth.

The Bua vein is a fissure in andesite. It is from 1 to 1.5 meters in width. Bands of manganese oxide make up the greater part of the vein in the upper workings, but in places solid compact bands of calcite are found. With depth, the manganese decreases, while the calcite increases until it makes up the major portion of the vein. The ore contains some rhodochrosite and from 2 to 6 per cent iron pyrite. The highest values are near the outcrop, and are usually found in the manganese bands. These values decrease with depth.

The Eastern mine, Aroroy, Masbate, has a very wide vein with large amounts of quartz, stained with iron oxide and manganese oxide in the upper workings. In places it appears honeycombed, and stained with black manganese. Very little calcite is found in the upper level, but it increases with depth until on the 60-meter level the vein is composed almost entirely of calcite. On the 30-meter level the vein is about half calcite and half quartz, and contains from 3 to 8 per cent iron pyrites. The gold values are highest near the outcrop, and are found in iron- and manganese-stained quartz.

The Colorado deposit is made up of honeycombed quartz stained with iron and manganese, crossed irregularly by bands of hard, flinty quartz and bands of soft manganese. The banding is very pronounced and in places is very much twisted as if movement had taken place in the vein producing lines of weakness, but generally it is parallel to the walls. The honeycombed quartz has formed molds representing perfect calcite crystals and cleavage, as if at one time calcite had formed the major portion of the gangue. In the lowest workings some calcite has been encountered. The gold values are highest near the outcrop, and decrease with depth.

In all of these examples the richest ore is at or near the surface, and the values found so far appear to decrease with depth. This condition would tend to indicate that no solution, or only an insignificant amount of solution, had taken place due to the chlorine reaction. All of these deposits are in regions of rugged relief and heavy rainfall, so that erosion would naturally be very rapid, and placer deposits would be expected in all cases. In most of these veins where the values are highest, from 20 to 30 per cent of the gold can be recovered by amalgamation. The characteristics of deposits where leaching by the solution of gold with free chlorine has taken place are a barren zone near the surface and a zone of enrichment near the water level. Neither of these features is present in the deposits cited. It is probable that a slight impoverishment occurs at the outcrop, due to the mechanical transportation of the fine gold along the numerous cavities and passages left by the leaching of the calcite.

ENRICHMENT IN CALCITE VEINS

While chemical concentration has apparently not taken place, it is evident that concentration of some character has occurred extensively, possibly to a greater extent than in a calcite-free ore deposit. This is due to the great solubility of calcite in leaching waters and particularly those containing carbon dioxide.

Enrichment, therefore, is caused by two conditions: (1) By the leaching of the calcite, which causes a removal of a valueless element, leaving a smaller mass of richer ore; and (2) by mechanical concentration of fine gold along channels caused by fracturing and by the removal of the calcite.

The removal of the calcite reduces the mass of the ore carrying the gold from 30 to 75 per cent. This alone would increase the value of the ore from 50 to 300 per cent. Certain portions of the veins in the Eastern and Colorado mines have been so thoroughly leached of calcite that the network of quartz remaining has the appearance of a sponge. The removal of the calcite and the oxidation of the pyrite in the quartz and the pyrite originally with the calcite but left behind in the leaching process creates an ideal condition for mechanical concentration of the fine gold in the primary ore. The gold is carried down with the manganese and iron oxides by water, and deposited along the cracks and fissures in the vein. The manganese being difficultly soluble and being so abundant in the ore is concentrated in large amounts simultaneously with the gold, forming soft black bands. This would account for the association of high gold values with the manganese.

Some of the examples of deposits in the United States cited by Emmons,[7] which seem to bear directly on points under discussion and to confirm these conclusions, are given below.

II. *Black Hills, S. D.*—The principal minerals are quartz, dolomite, calcite, pyrite, arsenopyrite, and gold * * *. Some of the ores at the surface were below the average tenor, while other surface-ores were two or three times as rich as the average * * *. In general, according to S. F. Emmons, secondary enrichment by surface-leaching has had relatively small importance.

III. *Treadwell Mines, Alaska.*—The minerals include quartz, albite, rutile, chlorite, * * * epidote, * * * chalcopyrite, and molybdenite. Manganese-minerals are not reported. * * * Nothing in the character of the ore indicates any important concentration of values by oxidizing waters.

VII. *Ophir District, California.*—The gangue is mainly quartz with a little calcite. * * * The extensive development of placers, the value of the ore near the surface, and the occurrence of valuable ore-shoots just below the surface are opposed to the notion of extensive migration of gold in these deposits.

IX. *Phillipsburg, Mont.*—At the Cable mine the deposits are included in a long, thin block of limestone in contact on either side with quartz-monzonite. The principal minerals are calcite, quartz, pyrrhotite, pyrite, magnetite, and chalcopyrite, with chlorite, muscovite, and other silicates. At one or two places small traces of manganese dioxide have been noted

[7] *Opus cit.*, 818 to 836.

in the oxidized ore, * * *. This deposit yielded important placers. Good ore was found at or very near the surface; and, according to the best obtainable data, the values increased somewhat for a short distance below the surface. Some concentration has taken place by the removal of calcite and other valueless material more rapidly than gold; but there is no evidence of secondary enrichment in gold below the water-table. The indications are that the gold has not been extensively transported since the deposit was formed.

XIII. *Georgetown, Colo., silver-lead deposits.*—The principal metallic minerals are argentiferous galena and blende, with pyrite and chalcopyrite; the ores usually carry about $2 gold per ton. * * * The gangue is quartz, chalcedony, barite, with carbonates of lime, iron, manganese, and magnesia. * * * The zone of complete oxidation extends from 5 to 40 ft. below the surface. The oxidized ore often contains several hundred ounces of silver per ton. Below this ore are friable black sulphides and secondary galena. This secondary ore, according to Spurr and Garrey, is rich in silver and lead, and carries more gold than occurs at greater depth.—Quoting from Spurr and Garrey:

* * * These richer ores diminish in quantity as depth increases, though gradually and irregularly, so that the lower portion of the veins contains relatively less silver and lead. The best ore in most veins has been found in the uppermost 500 feet, * * *.

XIV. *Auriferous deposits of the Georgetown Quadrangle, Colorado.*— They carry pyrite, chalcopyrite, * * * quartz, adularia, and gold, with minor amounts of barite, fluorite, telluride, etc. Carbonates of iron, magnesium, lime, and manganese occur, but are relatively rare. * * * They have yielded some moderately-productive placers. In several mines, the oxidized is much richer than the average ore.

XVI. *Cripple Creek, Colo.*—* * * Calaverite is the chief primary constituent; native gold is rarely present in the unoxidized ores. Pyrite is widely distributed; tetrahedrite, * * * and molybdenite are sparingly present. The gangue is quartz, fluorite, adularia, carbonates (including rhodochrosite), some sulphates, etc. Some of the deposits were workable at the surface, but the placers which have formed are relatively unimportant. * * * Manganese oxides are often present in the oxidized zone, and, according to Penrose, form nodules in the Pharmacist and Summit mines. They result from the alteration of rhodochrosite, manganiferous calcite, or other minerals, and are generally distributed in the oxidized zone as stains filling cracks and fissures. * * * Whether a slight enrichment of gold has taken place in the oxidized zone it is not easy to decide. Lindgren and Ransome are inclined to the belief that the oxidized zone as a whole is somewhat richer than the corresponding telluride zone. If this is true, no extensive downward migration of gold can have taken place. The trivial enrichment in the oxidized zone may have resulted from the removal of some constituents of the primary ore.

XX. *Tonopah, Nev.*—The deposits at Tonopah, Nev., are silver-gold replacement-veins in andesite. * * * Placers are not developed. The primary ore, according to J. E. Spurr, is composed of quartz, adularia, sericite, carbonates of lime, magnesia, iron, and manganese, with argentite, stephanite, polybasite, chalcopyrite, pyrite, galena, blende, silver selenide, and gold in an undetermined form. * * * The waters which descend through the oxidized zone carry sulphates and chlorides, and "wad"

is plentiful; but judging from the fairly constant proportion of gold to silver (about 1 to 100 by weight) there has been little selective migration of gold and silver during oxidation, although the vein has been enriched to some degree by downward penetration of minerals leached from the outcrop as it was eroded.

XXII. *Manhattan, Nev.*—Although the schists contain stringers of gold of uncertain genesis, the principal deposits are steeply-dipping lodes of quartz and calcite, stained with iron and manganese oxides. Some placers are developed. Rich ore was found very near the surface, but it was richer a few feet below the outcrop than at the surface. * * * In many instances the gold of the pockets of rich ore is intimately associated with iron and manganese oxides.

XXIV. *Bullfrog District, Nevada.*—The minerals include pyrite, quartz, and manganiferous calcite. Enough manganese is present in the calcite to stain much of the oxidized ore chocolate-brown or black. No placers are developed. The outcrops are comparatively poor, but within a few feet of the surface good ore was encountered, and some of the deposits were worked by open-cut. Some of the deposits decreased in value l `ow the 400-ft. level, where ore carrying less than $5 per ton is encountered. Since the ore above this level carried many times this value, it appears that there has been a secondary concentration by surface-waters, and that the rich ore is related to the present topographic surface.

GOGO, ENTADA SCANDENS BENTHAM, AND ITS EFFECT ON GOLD AND GOLD SOLUTIONS

By F. T. EDDINGFIELD

(*From the Division of Mines, Bureau of Science, Manila, P. I.*)

Since in the Philippines *gogo* juice has been universally used by the natives in panning gold-bearing sands, an investigation of its properties seemed desirable. The native has for panning a large wooden bowl, *batea,* which is about 65 centimeters in diameter, and slopes to a point in the center like a very flat inverted cone. The panner, usually a woman, has a little gogo bark at hand which at certain times she squeezes over the pan, causing the juice to fall on the water in the pan. It is believed that in this way more gold is recovered, by causing the fine gold to settle quickly and not float away.

According to Bacon,[1] gogo is taken from the plant *Entada scandens* Bentham. It is called "gogo" by Tagalogs and "bayogo" and "balogo" by the Visayans and Pampangans. The solution obtained from gogo is neutral, neither acid nor alkaline. Its chief constituent is saponin, a complex vegetable poison, which has a very slight acid reaction, and constitutes one of the groups of glucosides. These are generally colloids. Bacon further states that saponin has the quality of holding bodies in suspension; such as powdered charcoal, lead sulphide, barium sulphate, and barium carbonate; and that mercury is readily "killed" and oils emulsified by its aqueous solutions. In the following pages the aqueous solutions of gogo bark will be referred to as "gogo."

Several tests were made with mercury, and it was noted that when gogo was added the mercury was easily divided into minute globules which refused to be reunited. This is caused by a thin film being formed around each globule which "soils" it and makes it difficult for fresh faces of mercury to come in contact with each other. It also robs the mercury of its quality of amalgamation with gold, silver, and copper; a condition which has probably given rise to the belief, held by some, that Paracale gold will not amalgamate.

[1] *This Journal* (1906), 1, 1022.

In order to obtain finely divided gold, gold chloride solution was treated with oxalic acid. While this precipitate was still in suspension, gogo was added. It had apparently no effect upon the physical condition of the gold, which settled with the same rapidity and had the same color as gold precipitated by oxalic acid alone.

Further tests were made to determine if gogo in any way increased the adhesion between gold and wood or the cohesion between gold particles, but no change was noted. It also failed to reduce the surface tension of water to any noticeable extent, or to clean the gold by cutting the oil upon it.

The above tests show that gogo has no qualities which would be beneficial to the concentration of gold and it would be actually harmful where amalgamation is used. Apparently its only agency is the effect of the spray of solution falling on the floating particles of gold in the pan and causing them to sink. Water sprayed in the pan would have the same effect. On the other hand, the tests indicated that gogo is detrimental where amalgamation is used, and its only apparent quality is to hold fine particles in suspension, an effect just opposite to that desired.

In making the test on finely divided, precipitated gold it was found that if gogo were added to the gold chloride solution before oxalic acid, or before precipitation had taken place, purple solutions were obtained which appeared to be colloidal gold. While such an investigation rightly belongs in the field of physical chemistry, it was decided to make a few tests on the formation of colloidal gold solutions by means of gogo, with the hope that they might prove of value as a basis for a more thorough research.

Zsigmondy [2] states in regard to forming colloidal gold, that—

the chief essential is distilled water of sufficient purity, and the absence of electrolytes is not so essential as the absence of colloids. Traces of the former will do no harm, seeing that a certain quantity of them is introduced into the water by the reagents themselves. On the other hand, traces of colloids, almost always present in all commercial distilled water, completely prevent formation of bright red gold hydrosols.

Therefore, it was interesting to discover that colloidal gold solutions could be made in the presence, and by means, of colloids.

The gogo was extracted from the gogo bark, which is obtained commercially in the Philippine markets, by allowing the bark to soak thoroughly in distilled water for five or ten minutes and

[2] Colloids and the Ultra-microscopic. 1st ed., J. Wiley & Sons, N. Y. (1909), 124.

squeezing out the solution. The solution is of a brown to reddish color, which gradually turns upon standing to a deep reddish brown. It was found that, if exposed to the air, large numbers of bacilli belonging to the *Bacillus proteus*[3] group were developed in the solution, and probably acted as reducing agents, producing different chemical compounds. It was also found that a mold (*Penicillium* sp.) grew prolifically on the surface of the solution. This fungus Bacon[4] states "decomposed the solution, causing the separation of sapogenin, carbon dioxide at the same time being given off." However, sterilized solutions of gogo undergo certain changes if allowed to stand for a sufficient length of time, giving results similar to those obtained by solutions in which bacilli have been developed.

The first experiment was made with freshly made gogo juice. One cubic centimeter of gold chloride solution, obtained by dissolving 1 gram of crystallized gold chloride in 100 cubic centimeters of distilled water, was placed in a test tube; 1 cubic centimeter of concentrated oxalic acid and a slight excess of gogo were added. The solution was thoroughly shaken and heated over a Bunsen burner. A deep purple solution was formed which remained practically unchanged upon standing. Freshly made gogo without the oxalic acid merely caused the formation of a brown precipitate. Purple solutions were also obtained by first boiling the gogo or the gold chloride solution with calcium carbonate or sodium carbonate, using the same proportions of solution. Several different colors were produced during these tests which were probably caused by various other organic compounds in the gogo. One was a black suspension of fine particles, which settled out completely at the end of ten days. Another was a slate-colored suspension which settled after five days. The characteristics of these precipitates were not determined. After the gogo had been allowed to stand for several days either in a sterile condition, or exposed to the air and the action of the bacilli or fungi, beautiful red solutions were obtained by adding from 2 to 6 cubic centimeters of gogo to 1 cubic centimeter of gold chloride solution and boiling. This solution remained practically unaltered upon standing, although diminution of the color was noted in the top of the test tube after a few weeks. The exact character of these reactions is too complex for so brief an investigation.

[3] Determined by Liborio Gomez, Bureau of Science.
[4] *Loc. cit.*

Another set of experiments was carried on by using pure saponin powder. A saturated solution of saponin in water was made. One cubic centimeter of gold chloride was placed in a test tube with saponin solution and boiled over a Bunsen burner. By variations in the amount of gold and saponin present, and by variations in the intensity of the heat applied, colors ranging from dark blue to purplish red were obtained. All of these suspensions settled out in from twenty-four to seventy-two hours. It was noted that the colors always changed gradually, through their various shades, to a dark blue, before settling.

Another test was made by placing 1 cubic centimeter of gold chloride solution in a beaker, adding 5 cubic centimeters of water, and boiling. To the boiling solution was added about 0.1 gram of saponin powder, which, upon further boiling, became a beautiful clear red. This also, upon standing, changed through the various purples to dark blue, and finally settled after seventy-two hours. It was found that if the gold chloride solution contained excess of acid, none of these reactions occurred. In such case sodium carbonate had to be added to neutralize the acid. By adding a few drops of sodium carbonate to 1 cubic centimeter of gold chloride and then adding saponin powder or gogo, various shades of red and purple were obtained which remained unchanged upon standing. The reds were particularly clear and deep. The application of heat seemed to be essential in all cases.

Microscopic examination was made to determine whether or not the solutions contained suspended metallic particles. By concentrating the rays of a strong arc light upon a thin film of solution placed upon a glass plate, the metallic particles could easily be distinguished in all of these solutions. It was noted that all of the purple and violet solutions had the same color by reflected and transmitted light, but only a few of the red solutions exhibited this characteristic; others, while showing beautiful clear colors by transmitted light, gave a brownish, muddy color by reflected light.

It appears from these experiments that the red hydrosols represent the finest particles of gold, and the deep blue the largest particles since the red changed to blue before complete precipitation. Whether this is due to a growth of the particle by continued precipitation or the joining together of particles was not determined. Furthermore, the finest particles would permit the passage of longer wave lengths of light than the larger particles; this would mean that the largest particles would transmit

colors in the violet part of the spectrum and the finest particles in the red.

The most interesting feature is the formation of colloidal gold solutions by means of a colloid (saponin) and in the presence of an electrolyte (oxalic acid), the two factors claimed by Zsigmondy to prevent its formation.

SUMMARY

Colloidal gold can be formed by—

Gold chloride, fresh gogo, and oxalic acid, plus heat.
Gold chloride and gogo (after standing), plus heat.
Gold chloride, gogo, and calcium carbonate, plus heat.
Gold chloride, gogo, and sodium carbonate, plus heat.
Gold chloride, saponin solution, and sodium carbonate, plus heat.
Gold chloride, saponin powder, and sodium carbonate, plus heat.

Suspensions which have colors similar to those of colloidal gold can be made by gold chloride and saponin alone plus heat, but these settle quickly.

THE COMPOSITION OF VARIOUS MILKS AND THEIR ADAPTABILITY FOR INFANT FEEDING

By FRANCISCO AGCAOILI

(*From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.*)

One plate

One of the most important factors responsible for the excessive death rate among Filipino children is found in the quality of milk frequently employed to nourish small children. The supply of fresh cow's milk is very limited throughout the Philippines generally, and recourse cannot therefore be had to this common substitute for the natural milk of the mother. The milk of goats can be obtained in some localities, but the supply is far too small to alleviate the situation. This is especially unfortunate, as the goat has been found of great value in tropical countries, the child obtaining its food directly from the animal in many cases, thus avoiding all danger from outside contamination of the milk (Plate I).

Carabao milk is abundant, but not well suited for young children. The fat content is very high, and the milk shows a marked tendency to form large curds. It is seldom found on the market in an unadulterated condition, and is rarely collected in a sanitary manner. It may safely be said that all fresh milks available at prices within reach of the poorer classes are highly dangerous owing to bacterial contamination, and should never be employed as food, especially for children.

The choice of a substitute for mother's milk is thus confined to various canned milks and prepared infant foods which are available in a satisfactory condition and at a reasonable price. During the past five years the Bureau of Science has had occasion

to analyze many hundred samples of these sterilized and condensed milks, and the average results thus obtained should be of considerable utility in aiding both mothers and physicians properly to adapt the various brands for infant feeding. The problem of modifying or altering a milk to make it approximate the composition of mother's milk is not difficult. The basis of any scientific modification must rest on the proportions of fat, carbohydrate, and protein present in the original milk as compared with normal mother's milk. It, therefore, becomes necessary to have data concerning the many brands of milk suitable for the purpose, and this information is recorded in the following tables. The composition of various fresh milks is shown in Table I.

TABLE I.—*Composition of fresh milks obtained in Manila.*

Type of milk.	Specific gravity.	Water.	Fat.	Lactose.	Protein.	Ash.	Number of samples analyzed.
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	
Human:							
Maximum_____	1.0360	91.48	9.97	11.21	2.76	0.72	_____
Minimum _____	1.0260	81.50	.88	2.50	.13	.01	a 151
Mean_____	1.0327	87.58	3.77	7.03	1.43	.20	_____
Carabao, pure:							
Maximum_____	1.0418	82.39	15.95	5.15	6.51	.91	_____
Minimum _____	1.0307	73.40	5.99	3.22	5.01	.77	7
Mean_____	1.0366	79.68	9.60	4.60	5.68	.83	_____
Carabao, high-grade market:							
Maximum_____	1.0400	89.43	28.40	9.95	10.00	1.07	_____
Minimum _____	.9030	61.04	4.28	.85	1.30	.24	213
Mean_____	1.0334	80.57	9.56	4.66	4.74	.71	_____
Carabao, low-grade market:							
Maximum_____	1.0400	97.80	8.90	6.90	5.50	.28	_____
Minimum _____	1.0100	83.19	1.35	.10	.34	.17	125
Mean_____	1.0200	89.57	4.69	2.64	2.75	.44	_____
Goat:							
Maximum_____	1.0360	87.97	6.80	5.87	4.70	.80	_____
Minimum _____	1.0280	84.90	3.24	3.31	2.29	.59	11
Mean_____	1.0304	86.69	5.02	4.34	3.29	.60	_____
Cow:							
Maximum_____	1.0350	90.59	7.63	6.05	4.55	.77	_____
Minimum _____	1.0170	84.38	1.64	2.39	6.05	.82	25
Mean_____	1.0300	87.74	3.79	4.60	3.18	.64	_____
Cream Australian dairy __	_____	56.03	40.65	.78	2.00	.54	2

a These extreme variations are due in part to the physical condition of the mother. In those cases where the calorific values are very low, the abnormal milk is generally due to insufficient nourishment of the mother. The age of the chilld also affects the composition of the milk. See Musgrave, *This Journal,* Sec. B (1907), **2,** 380.

The composition of various brands of sterilized natural milk is shown in Table II.

TABLE II.—*Composition of sterilized natural milks.*

Brand.	Analyses.	Water.	Fat.	Lactose.	Protein.	Ash.
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Milkmaid	20	87.29	3.68	5.11	3.24	0.68
Bear	15	87.14	3.70	5.22	3.25	.69
Natura	8	87.51	3.68	4.88	3.28	.65
Fussel's Green Butterfly	6	87.20	3.78	4.98	3.37	.67
Jura	4	87.64	3.71	5.01	3.06	.58
Dragon	4	87.49	3.62	5.00	3.31	.58
Vaca	2	87.65	3.39	5.09	3.24	.63
Flying Tiger	2	88.02	3.24	4.89	3.19	.66
Union	2	88.03	3.53	4.75	3.07	.62
Manoc	3	89.29	3.13	4.39	2.62	.57
Conqueror	2	88.19	3.28	4.87	3.04	.62
Bacchus Marsh	2	87.69	3.81	4.74	3.15	.61
Rowboat	1	88.82	2.97	4.72	2.94	.55
Swimmer	2	88.58	3.17	4.80	2.77	.68
Champion	1	87.82	3.21	5.26	3.02	.69
Elks	1	88.14	3.87	4.36	3.04	.59
Dutch Girl	1	87.77	3.32	5.18	3.07	.66
Anchor	1	88.08	3.60	4.35	3.33	.64
Dahl's	1	87.25	3.43	5.04	3.59	.69
Golden Cow and Calf	1	87.65	3.56	5.06	3.15	.58
Eury	1	86.46	4.98	4.10	3.77	.69
Nutricia	2	87.79	3.29			
Victoria	1	88.29	2.89			
Vacca Melk	1	87.97	3.30			
Golden Harp	1	87.60	3.70			
Gruyere	1	88.15	3.74			
White Swan	1	87.60	4.04			
Tropic Proof	1	89.00	2.14			
Obotritia	1	86.17	5.33			
Mont Seny	1	89.15	1.94	5.19	3.04	.68
Gu La	1	87.63	2.82	5.82	3.11	.62
Locati-Triulzi Co	1	86.40	4.05	4.77	4.08	.70
Berna	1	88.29	3.35	5.11	2.67	.58

The composition of various brands of unsweetened condensed milk is shown in Table III.

TABLE III.—*Composition of unsweetened condensed milks.*

Brand.	Analyses.	Water.	Fat.	Lactose.	Protein.	Ash.
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Milkmaid	10	67.89	9.70	13.26	7.44	1.71
Bear	6	67.26	9.75	12.86	8.37	1.76
Highland	6	72.75	7.75	10.45	7.45	1.60
Alpine	6	72.08	8.55	10.74	7.21	1.42
Peerless	6	71.99	8.60	10.50	7.36	1.55
Libby's	7	73.55	8.34	9.66	7.21	1.24
Every day	6	74.21	8.30	9.54	6.57	1.38
Fussel's Silver Butterfly	6	66.78	9.48	13.71	8.63	1.40
Cow's head	3	63.69	10.05	15.07	9.17	2.02
St. Charles	5	71.30	8.17	10.44	8.31	1.78
Mount Vernon	3	70.25	9.46	10.26	8.60	1.43

TABLE III.—*Composition of unsweetened condensed milks*—Continued.

Brand.	Analyses.	Water.	Fat.	Lactose.	Protein.	Ash.
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
St. George	4	78.91	6.67	7.38	5.79	1.25
Cascade	1	73.95	8.78	9.57	6.50	1.20
Silver Cow	1	70.72	8.80	11.20	7.98	1.30
Bacchus Marsh	2	69.74	10.42	10.35	8.49	1.00
Milkina	1	71.02	8.80	10.33	8.42	1.43
Sego	1	69.92	9.78	11.68	7.10	1.52
Battleship	1	71.50	7.20	10.29	9.51	1.50
Lily	1	71.82	11.44	8.54	6.69	1.51
Viking	1	68.95	8.24	---------	---------	1.45
Milka Alpina	1	64.35	10.64	---------	---------	1.90
Pioneer	1	73.62	9.26	---------	---------	---------
Globe	2	70.39	9.59	---------	---------	---------
Natura	2	69.13	8.18	---------	---------	---------
Hollandia	1	65.75	7.83	---------	---------	---------
Rizal Day	1	74.32	6.13	---------	---------	---------
Domestic	1	72.30	5.50	13.40	7.20	1.60
Harmens	1	67.10	8.90	---------	---------	---------
Carnation	1	73.89	7.42	---------	---------	---------

The composition of various brands of sweetened condensed milk is shown in Table IV.

TABLE IV.—*Composition of sweetened condensed milks.*

Brand.	Analyses.	Water.	Fat.	Lactose.	Protein.	Ash.	Sucrose.
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Milkmaid	16	22.30	9.80	14.87	8.84	1.92	42.27
Gold Seal	6	19.27	9.94	15.74	8.98	1.83	44.24
Bacchus Marsh	5	22.01	11.24	12.53	9.45	1.75	43.02
Standard	6	21.80	9.60	15.90	9.00	1.70	42.00
White Star	3	23.30	9.24	16.04	9.74	1.68	40.00
Red Gate	1	27.25	7.92	12.19	10.29	.1.90	40.45
Dutch Girl	1	25.40	9.85	10.50	8.94	1.82	43.49
Red Cross	2	30.60	8.50	11.91	7.35	1.55	40.09
Lion	2	24.93	9.00	7.86	8.37	1.84	48.00
Fussel's Red Butterfly	2	21.24	9.13	15.50	9.20	1.93	43.00
Natura	1	22.17	9.25	---------	---------	---------	36.50
Libby's	3	26.59	8.38	15.11	7.59	1.64	40.69
Emery	1	25.69	9.00	---------	---------	---------	42.63
Lowood	1	26.65	8.80	9.11	8.86	1.86	44.72
Hollandia	1	27.33	11.00	---------	---------	---------	42.56
Valkyrie	1	22.77	12.96	11.13	8.91	1.83	42.40
Silver Churn	1	29.95	9.79	13.51	3.90	1.35	41.50
Luzon	1	13.20	11.00	---------	---------	---------	49.38
Nurse	1	20.05	7.75	18.62	7.65	1.73	44.20
Gruyere Castle	1	28.04	5.04	10.16	8.70	1.55	46.51
Republic	1	23.32	9.60	---------	.	45.00
Harbour	3	29.09	9.41	---------	---------	1.77	41.47
Swiss Farm	1	28.90	9.80	---------	---------	---------	39.07
Eagle	10	22.40	9.11	13.78	8.05	1.49	45.17
Flag	1	21.95	10.13	15.94	9.01	1.81	41.16
Berna	1	19.31	10.13	17.20	10.00	1.32	42.04
Bear	2	19.64	9.25	19.78	8.92	1.72	41.25

The composition of various brands of sweetened condensed skimmed milk is shown in Table V.

TABLE V.—*Composition of sweetened condensed skimmed milks.*

Brand.	Analyses.	Water.	Fat.	Lactose.	Protein.	Ash.	Sucrose.
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Imperial Dove _____	3	24.18	traces.	17.40	9.78	2.01	46.63
Royal _____	1	23.16	traces.	17.17	10.17	2.14	47.36
Heron_____	2	21.32	0.88	16.86	9.98	2.41	48.55
Volunteer_____	1	29.70	traces.	10.92	10.63	2.00	46.75
Star_____	1	21.70	0.38	17.68	9.19	1.98	49.07
Pigeon _____	1	26.64	_____	_____	_____	_____	43.41
Buttler _____	2	16.85	traces.	22.68	10.10	2.31	48.06
Windmill_____	1	_____	_____	_____	_____	_____	48.72
Rizal_____	2	24.45	traces.	_____	_____	_____	54.20
Tiger _____	1	21.25	traces.	_____	_____	_____	
Axe_____	1	15.02	traces.	27.97	9.89	2.05	45.07

The composition of various brands of cream and dried milk is shown in Table VI.

TABLE VI.—*Composition of creams and dried milks.*

Brand.	Analyses.	Water.	Fat.	Lactose.	Protein.	Ash.
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Milkmaid _____	10	64.74	23.07	3.52	2.90	0.77
Bear_____	6	57.52	37.61	2.36	2.09	.42
Dragon _____	3	69.49	22.50	4.71	2.76	.54
Fussel's Golden Butterfly _____	3	62.38	31.23	3.54	2.38	.47
Lion _____	1	64.65	32.40	.55	2.05	.35
Valkyrie_____	1	63.04	30.60	2.88	2.80	.68
Dahl's _____	1	70.90	21.60	4.12	2.89	.49
Sahne _____	1	81.07	11.90	3.59	2.98	.46

DRIED MILK.

Trumilk _____	2	1.70	31.67	35.05	27.65	3.93
3–C _____	4	3.07	24.44	52.05	15.50	4.94

METHODS FOR MODIFYING MILK

The most convenient method possible for modifying cow's milk is to dilute it with the correct amount of pure water, but the result is never a very close approximation to mother's milk since the proportions of the various constituents are not altered by the addition of water. In many cases a more exact modification is desirable, though seldom closer than to 0.1 per cent, and numerous tables have been devised whereby this result may be obtained.

The proportion of sugar is greater, and that of protein considerably less, in mother's milk than in cow's milk. This may be seen from Table VII.[1]

TABLE VII.—*Comparative average composition of cow's milk and mother's milk.*

	Woman's milk, average.	Cow's milk, average.
	Per cent.	*Per cent.*
Fat	4.00	4.00
Sugar	7.00	4.50
Proteids	1.50	3.50
Salts	.20	.75
Water	87.30	87.25
	100.00	100.00

The addition of cream and milk sugar or lactose to diluted cow's milk is, therefore, necessary to effect a proper balance. The amount of each of these constituents may be calculated from analyses of the original milk and cream by a simple formula. An actual case for which the data are contained in Table VIII may serve to illustrate the method.

TABLE VIII.—*Data for modifying cow's milk.*

	Fat.		Sugar.		Protein.	
	Per cent.	*Gram per cc.*	*Per cent.*	*Gram per cc.*	*Per cent.*	*Gram per cc.*
Milk desired	4.00	0.040	7.00	0.070	1.00	0.0100
Original milk	3.60	.036	5.10	.051	3.30	.033
Original cream	28.40	.284	3.90	.039	2.90	.029

The proportion of cream that should be added to the original milk may be found from two equations based upon their fat and protein content. Let $M =$ number of cubic centimeter milk and $C =$ number of cubic centimeter cream required. Then the milk used will contain 0.036 M gram of fat and 0.033 M gram of protein, and the cream added to it will supply 0.284 C gram of fat and 0.029 C gram of protein. Therefore, 100 cubic centimeters of the modified milk containing 4 grams of fat and 1 gram of

[1] Holt, L. E., The Diseases of Infancy and Childhood. D. Appleton and Company, New York and London (1910), 185.

protein corresponding to mother's milk must be made from the volumes of milk and cream necessary to satisfy the equations:

$$0.036 \text{ M} + 0.284 \text{ C} = 4$$
$$0.033 \text{ M} + 0.029 \text{ C} = 1.$$

Solving for M and C gives 20.1 cubic centimeters of milk and 11.7 cubic centimeters of cream as the requisite volumes to employ. The amounts of fat, sugar, and protein contributed by the milk and cream are shown in Table IX. A chart for the composition of these is given by Cox.[2]

TABLE IX.—*Data for modifying cow's milk, continued.*

Source.	Fat.	Sugar.	Protein.
	Grams.	*Grams.*	*Grams.*
20.1 cc milk _____	0.72	1.02	0.66
11.7 cc cream _____	3.32	.46	.34
Total_____	4.04	1.48	1.00

This mixture contains the proper amounts of fat and protein when diluted to 100 cubic centimeters, but the total lacks 5.519 grams of sugar that must be added in the form of milk sugar or lactose. The amounts of the various constituents have been recorded to the second decimal place merely to simplify their derivation, although the requirements in practice would naturally demand less accuracy.

The total amount of the resulting modified milk that should be allowed a child during twenty-four hours for its nutrition and proper development may be approximated by considering the calorific value of the food. This is computed from the fat, protein, and sugar content with individual calorific values of 9.3, 4.1, and 4.1 calories per gram, respectively. The value of 1 cubic centimeter of the modified milk as obtained above would thus be 0.704 calory. Holt[3] gives the following data for determining the volume of milk necessary for a child. Divide the weight in grams of the child by 10, and the quotient by the food value in calories of 1 cubic centimeter of the milk. The result gives the number of grams of milk required to supply the necessary calories for twenty-four hours. In the case of a child of one

[2] Musgrave, W. E., *This Journal, Sec. B* (1907), **2**, 382.
[3] *Loc. cit.*

month, weighing 4 kilograms, and fed ten times a day on the above modified milk, the rule gives $\dfrac{4000}{10 \times 0.704} = 568.18$ cubic centimeters, or 56.8 cubic centimeters for each meal. This may be diluted with pure water according to the capacity of the child's stomach.

The tables of analyses included in this paper make it possible to modify properly any of the numerous brands of milk available, and should assist in encouraging scientific feeding and the reduction of infant mortality due to ignorance or neglect of a few simple principles of pediatrics.

ILLUSTRATION

PLATE I. Showing baby feeding directly from a goat. (By the courtesy of La Gota de Leche.)

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PLATE I.   BABY FEEDING FROM A GOAT.

THE COMPOSITION OF CARABAO'S MILK

By E. R. Dovey

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With the possible exception of goat's milk, carabao's milk is the principle native dairy product in the Philippine Islands. Its use is almost wholly restricted to the native population. The milk has long been known to be very rich as compared with cow's milk, resembling the milk of other kinds of buffalo in this respect, but its composition has been little studied. Although many analyses of buffalo's milk have been published from time to time, it is a regrettable fact that in many cases the species of animals from which the milk was obtained is unrecorded. The average results obtained by several workers who have examined the milk of various species of buffalo are given in Table I.

TABLE I.—*Analyses of buffalo's milk.*

Kinds of buffalo.	Samples.	Analyst.	Total solids.	Fat.	Protein.	Sugar.	Ash.
			Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Unknown		Fleischmann [a]	17.07	7.46	4.59	4.21	0.81
Egyptian (Gamoose).	16	Peppel and Richmond. [b]	15.9	5.56	3.86	5.41	1.03
Indian	18	Leather [c]	16.26	6.76	3.78	4.80	.75
Do	large number	Meggit and Mann [d]	18.27	8.11	4.33	5.00	.82
Unknown	1	Strohmer [e]	18.33	9.02	3.99	4.50	.77
Carabao	6	Bliss [f]	22.09	10.63	6.31	3.73	.88

[a] Blyth, Wynter, Foods, their composition and analysis. C. Griffin and Company, London (1910).
[b] *Trans. Journ. Chem. Soc.* (1890), **51**, 754.
[c] *Analyst* (1901), **26**, 40.
[d] *Mem. Indian Dept. Agr.* (1912), **2**, 195.
[e] *Chem. Centralbl.* (1888), III, **19**, 478.
[f] *This Journal, Sec. B* (1907), **2**, 371.

Table II shows the composition of carabao's milk on the Manila market, where adulteration is known to be practiced extensively.

TABLE II.—*Carabao's milk from Manila markets analyzed at the Bureau of Science, 1910–1912.*

		Water.	Total solids.	Fat.	Solids not fat.
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
1910.　84 samples	Maximum	97.80	27.21	16.02	15.27
	Minimum	72.79	2.20	1.78	.42
	Average	87.27	12.73	6.31	6.42
1911.　96 samples	Maximum	91.65	26.96	19.40	16.80
	Minimum	73.04	8.35	1.80	4.07
	Average	83.16	16.84	7.77	9.07
1912.　13 samples	Maximum	92.68	19.56	10.81	10.17
	Minimum	80.44	7.32	3.51	3.81
	Average	86.89	13.11	6.09	7.02

The object in view in undertaking the present work was to collect data to enable the local Board of Food and Drug Inspection to fix a standard for milk sold for public consumption. For this purpose it was decided to make complete and accurate analyses of a number of milks.

In obtaining the samples for these analyses, the carabao was milked dry under our supervision and the complete milking was thoroughly mixed and its volume measured. The milk was collected directly in a clean graduated glass, and transferred to stoppered bottles.

Owing to the high percentage of total solids, if a sample was allowed to stand overnight it would invariably be found in a clotted state in the morning. The most effective method for breaking up such a coagulum for analytical purposes was found to be shaking vigorously with steel balls.

In making the analyses, the milk fat was estimated by the Leffmann-Beam centrifugal method using Babcock bottles and 10 cubic centimeters of milk, the result being corrected by the factor 1.76. This result was confirmed by the Werner-Schmidt process, extracting five times and using the residue of fat for determining the butyro-refractometer reading. The total solids were determined directly on 10 cubic centimeters of milk, and the result confirmed by means of the Richmond formula from the percentage of fat and the specific gravity.

In determining the aldehyde figure, in every case after the second end point had been obtained a further addition of formaldehyde was made and a third end point obtained, which thus measured the acidity of the formalin in each estimation. The total protein and albumin were estimated in the usual way. Attempts to measure the albumin and casein separately by a modification of the process used for the aldehyde figure did not prove successful. The lactose was in every case estimated polarimetrically and checked by subtracting the sum of the fat, protein, and ash from the total solids.

The complete analyses of 19 authentic samples of pure carabao's milk are given in Table III.

TABLE III.—*Analyses of carabao's milk.*

	Sample No.—				
	1	2	3	4	5
Age of carabao_____years__	12	8	7	12	7
Age of calf_____months__	6	5	3	2.5	5
Total volume _____cc___	520	900	300	350	750
Specific gravity at 17°.5 C _____	1.0362	1.0374	1.0418	1.0307	1.0332
Water _____per cent__	78.42	82.39	82.39	73.40	80.44
Total solids:					
Direct _____do____	21.58	17.61	17.61	26.60	19.56
Calculated a _____do____	21.64	17.42	17.30	29.98	19.70
Fat _____do____	10.44	6.57	5.62	15.93	9.42
Solids, not fat _____do____	11.17	11.04	12.02	10.65	10.18
Proteins:					
Calculated _____do____	5.16	5.16	5.73	6.27	4.98
Direct (N × 6.25)_____do____	5.16	5.08	5.83	6.29	5.91
Casein _____do____	4.73	4.77	5.44	6.05	4.74
Albumin _____do____	.43	.31	.39	.24	.27
Lactose _____do____	5.17	5.20	5.32	3.55	4.22
Total ash _____do____	.840	.770	.865	.914	.786
Soluble ash _____do____	.150	.053	.170	.140	.080
Insoluble ash _____do____	.690	.723	.695	.774	.706
Alkalinity of ash _____do____	.002	.004	.002	.002	.004
Chlorides as Cl _____do____	.042	.028	.052	.056	.039
Calcium as CaO _____do____	.278	.250	.296	.299	.278
Phosphoric acid _____do____	.280	.260	_____	_____	.297
Acidity (as lactic)_____do____	.260	.260	.229	.216	.248
Aldehyde figure _____	30.2	30.2	33.5	36.7	29.1
Serum:					
Specific gravity at 20° _____	1.0345	1.0331	1.0323	1.0321	1.0290
Immersion refractometer at 20°_	43.8	43.3	43.0	42.8	40.2
Fat butyro-refractometer at 25°_____	49.2	50.0	49.7	51.1	50.0

a After the formula of Richmond.

TABLE III.—*Analyses of carabao's milk*—Continued.

	Sample No.—				
	6	**7**	**8**	**9**	**10**
Age of carabao_____years__	12	9	11	8	12
Age of calf_____months__	2	5	8	8	6
Total volume _____cc__	700	680	480	480	820
Specific gravity at 17°.5 C_____	1.0365	1.0399	1.0385	1.0386	1.0347
Water_____per cent__	80.20	80.50	73.24	79.99	72.15
Total solids:					
Direct _____do____	19.80	19.50	26.76	20.01	27.85
Calculated[a]_____do____	19.97	19.52	24.84	20.73	27.55
Fat _____do____	8.96	7.94	12.48	9.15	15.62
Solids, not fat _____do____	10.87	11.59	14.22	10.87	12.29
Proteins:					
Calculated_____do____	6.00	6.01	7.26	5.43	6.85
Direct (N × 6.25) _____do____	5.88	6.51	9.79	5.49	7.87
Casein _____do____	5.41	5.69	8.54	5.02	6.94
Albumin_____do____	.49	.82	1.25	.47	.93
Lactose_____do____	4.40	4.20	3.50	4.50	3.50
Total ash _____do____	.798	.840	.948	.875	.922
Soluble ash _____do____	.043	.024	.018	.021	.122
Insoluble ash _____do____	.755	.818	.930	.854	.800
Alkalinity of ash _____do____	.002	.002	.002	.002	.002
Chlorides as Cl _____do____	.000	.016	.017	.010	.028
Calcium as CaO _____do____	.267	.304	.342	.299	.314
Phosphoric acid _____do____	.323	.317	.372	.338	.347
Acidity (as lactic)_____do____	.272	.267	.315	.267	.189
Aldehyde figure _____	35.1	35.1	42.4	31.8	40.1
Serum:					
Specific gravity at 20° _____	1.0350	1.0325	1.0322	1.0337	1.0353
Immersion refractometer at 20°__	44.3	44.0	43.0	47.0	47.8
Fat butyro-refractometer at 25° _____	48.5	49.8	49.7	48.7	49.2

	Sample No.—				
	11	**12**	**13**	**14**	**15**
Age of carabao_____years__	15	10	7	10	11
Age of calf_____months__	9	11	2	6	4
Total volume _____cc__	1,060	350	750	600	600
Specific gravity at 17°.5 C_____	1.0374	1.0343	1.0390	1.0360	1.0344
Water_____per cent__	80.24	72.55	80.45	76.79	75.98
Total solids:					
Direct _____do____	19.76	27.45	19.55	23.41	24.02
Calculated[a]_____do____	20.04	27.62	19.79	23.82	24.50
Fat _____do____	8.82	15.75	8.20	12.27	12.87
Solids, not fat _____do____	10.94	11.72	11.28	11.14	10.84
Proteins:					
Calculated_____do____	5.07	5.64	5.38	4.85	5.20
Direct (N × 6.25) _____do____	5.62	5.43	5.62	5.27	5.66
Casein _____do____	5.23	4.81	5.08	4.80	5.19
Albumin_____do____	.389	.63	.54	.47	.47
Lactose_____do____	4.78	3.58	4.34	4.55	4.40
Total ash _____do____	.843	.903	.823	.834	.755
Soluble ash _____do____	.106	.100	.081	.120	.056

[a] After the formula of Richmond.

TABLE III.—*Analyses of carabao's milk*—Continued.

	Sample No.—				
	11	**12**	**13**	**14**	**15**
Insoluble ash _____per cent __	0.737	0.803	0.742	0.720	0.699
Alkalinity of ash _____do____	.005	.001	.002	.000	.000
Chlorides as Cl _____do____	.018	.048	.021	.042	.045
Calcium as CaO _____do____	.311	.308	.310	.278	.252
Phosphoric acid _____do____	.278	.308	.283	.312	.327
Acidity (as lactic)_____do____	.151	.213	.170	.165	.234
Aldehyde figure _____	29.7	33.0	31.5	28.4	30.4
Serum:					
Specific gravity at 20° _____	1.0353	1.0380	1.0382	1.0370	1.0368
Immersion refractometer at 20°__	46.0	48.8	48.0	48.1	48.2
Fat butyro-refractometer at 25°_____	48.9	49.7	48.5	50.4	50.6

	Sample No.—				
	16	**17**	**18**	**19**	**Average.**
Age of carabao_____years___	10	6	5	8	_____
Age of calf_____months___	5	6	1	4	_____
Total volume_____cc___	1,400	550	1,180	730	_____
Specific gravity at 17°.5 C_____	1.0377	1.0370	1.0360	1.0316	1.0864
Water_____per cent___	80.77	80.25	80.41	80.22	78.46
Total solids:					
Direct _____do____	19.23	19.75	19.59	19.78	21.55
Calculated a_____do____	19.66	19.93	20.17	19.87	21.59
Fat _____do____	8.49	8.80	9.01	9.81	10.35
Solids, not fat _____do____	10.78	10.93	10.34	9.92	11.20
Proteins:					
Calculated _____do____	5.12	5.49	4.49	4.57	5.50
Direct (N × 6.25) _____do____	5.65	5.65	5.18	4.86	5.88
Casein _____do____	5.19	5.16	4.66	4.44	5.35
Albumin_____do____	.46	.49	.52	.42	.53
Lactose_____do____	4.15	4.00	4.27	4.45	4.32
Total ash _____do____	.896	.818	.890	.710	.844
Soluble ash _____do____	.061	.110	.067	.110	.086
Insoluble ash _____do____	.835	.708	.823	.610	.758
Alkalinity of ash _____do____	.006	.001	.000	.004	.002
Chlorides as Cl _____do____	.021	.024	.021	.018	.029
Calcium as CaO_____do____	.350	.261	.260	.255	.274
Phosphoric acid _____do____	.331	.343	.334	.227	.310
Acidity (as lactic)_____do____	.155	.244	.216	.146	.222
Aldehyde figure _____	29.9	32.0	26.1	26.7	32.2
Serum:					
Specific gravity at 20° _____	1.0342	1.0380	1.0374	1.0304	1.0345
Immersion refractometer at 20°__	46.0	47.5	46.8	42.6	45.3
Fat butyro-refractometer at 25°_____	50.4	50.2	50.2	50.3	49.7

a After the formula of Richmond.

It will be seen by a consideration of the above figures that whereas in cow's milk the fat is approximately 30 per cent of the total solids, in the case of carabao's milk, it reaches nearly 50

per cent. The ratio of lactose, protein, and ash differs greatly from cow's milk, being about 5 : 7 : 1. This agrees approximately with the figures 5 : 6 : 1 obtained by Meggit and Mann [1] for the milk of Indian buffaloes. A very different ratio was obtained by Peppel and Richmond [2] for the milk of the Egyptian buffalo, their figures being 6 : 5 : 1. The percentage of lactose in carabao's milk is approximately the same as in cow's milk. The protein is much higher, higher in fact than in the milk of any buffalo.

Again, whereas the ratio of casein to albumin in cow's milk is as 1 : 7.5 and in the case of the Egyptian buffalo, 1 : 5.5, in the case of the carabao, it averages 1 : 10. However, the amount present fluctuates considerably as was found by the varying degree of ease with which an albumin-free serum was obtainable for the serum determinations.

The calculation of total solids by the Richmond formula, $T.\ S. = \dfrac{Q}{4} + \dfrac{6F}{5} + 0.14$, was found to give accurate results as is shown above, and is available for use if any large number of control analyses have to be made at any time. The determination of the total protein by means of the aldehyde figure using the common factor 0.171 was not so successful, and it would seem that better results might be obtained using the factor 0.181.

The total mineral matter shows about the same ratio to the solids not fat in carabao's as in cow's milk, but the ratio of phosphoric acid and calcium to ash is greater in the former than in the latter. As usual, the principal ash constituents are fairly constant, and a determination of the phosphoric acid [3] might be of assistance in examination of samples suspected of being watered, as confirmation of adulteration.

In order to confirm the above results, an estimation of fat and total solids was made on samples of genuine milk from 105 animals with the following result:

Constituent.	Maximum content.	Minimum content.	Average content.
	Per cent.	*Per cent.*	*Per cent.*
Milk fat	17.42	5.66	10.44
Total solids	28.70	15.84	21.42
Solids not fat by difference	15.16	8.68	11.28
Water	84.16	71.30	78.58

[1] *Mem. Indian Dept. Agr.* (1912), **2**, 195.

[2] *Trans. Journ. Chem. Soc.* (1890), **51**, 754.

[3] A new method of milk testing. *Analyst* (1908), **33**, 273.

These figures show that carabao's milk varies greatly in composition. However, in view of the above results, which are in close agreement with the more complete analyses given in Table III, it is recommended that a minimum of 8.5 per cent of solids *not fat* and 8.0 per cent of *milk fat* be adopted as the standard under the Food and Drugs Act.

CHEESE FROM CARABAO'S MILK

The milk of the carabao is not used for making butter in spite of its high fat content, owing to lack of knowledge regarding the use of butter and the difficulty of keeping it without ice in a warm climate. However, a kind of cheese is made by warming the milk, then coagulating the fat and protein by adding vinegar and salt. The whole is poured into bamboo tubes fitted with pistons by means of which the curd is compressed in the bottom of the tube and the whey is forced out through small apertures in the side or through the porous partition of the bamboo. The result is a small curd cake, about 4 centimeters in diameter, 1 centimeter thick, and weighing about 16 grams. It is white in color and tough in consistency, as might be expected from its mode of manufacture. It is incorrectly called cheese since no ripening process is allowed to take place.

The analyses of 3 samples of this cheese are given in Table IV.

TABLE IV.—*Percentage composition of cheese made from carabao's milk.*

Constituent.	Sample No.—		
	1	2	3
Moisture	51.55	50.00	56.00
Milk fat	27.14	28.91	29.37
Protein (N × 6.25)	15.52	15.17	15.71
Acetic acid	.112	.029	---------
Lactic acid	.195	.48	---------
Insoluble ash	1.48	1.64	1.76
Soluble ash	3.45	4.27	4.01
Sodium chloride	.43	0.447	---------
Fat butyro-refractometer reading at 25°	50.6	50.7	49.7

SUGAR-CANE EXPERIMENTS

By CLODOALDO TEMPONGKO [1]

(From the College of Agriculture, Los Baños, P. I.)

Sugar cane was being cultivated by the natives at the time Magallanes discovered the Philippine Islands in 1521, and has ever since supplied an important article of commerce. The yearly amount exported since 1817 is shown in Table I.

TABLE I.—*Sugar exported from the Philippine Islands.*[a]

Year.	Quantity.	Value.	Per cent of total value of exports.	Year.	Quantity.	Value.	Per cent of total value of exports.
	Kilos.	*Dollars.*			*Kilos.*	*Dollars.*	
1817	3,972,539			1883	196,834,584	10,546,185	45.83
1852	26,759,003			1884	122,128,325	6,013,982	30.33
1854	47,704,105	2,225,022	38.07	1885	204,222,480	8,646,735	42.18
1855	35,570,206	1,725,630	26.83	1886	184,939,549	7,016,848	34.90
1856	48,157,225	3,705,434	38.61	1887	171,752,248	6,153,511	31.66
1857	36,644,895	4,576,531	36.19	1888	160,987,894	6,274,385	32.32
1858	27,288,637	2,249,195	22.73	1889	228,468,878	9,098,543	35.45
1860	49,799,815	4,136,296	40.93	1890	144,841,483	7,266,798	33.72
1861	46,043,438	3,166,678	37.41	1891	138,217,635	5,698,949	27.29
1862	61,934,853	3,561,289	37.00	1892	252,798,196	7,766,326	40.54
1863	52,061,920	3,341,056	31.44	1893	261,522,201	10,370,574	46.63
1864	45,036,305	3,513,603	31.20	1894	210,646,386	5,474,422	33.11
1865	46,831,637	6,383,629	29.01	1895	341,469,556	6,068,485	32.22
1866	41,288,259	6,039,496	25.88	1899	85,827,565	3,458,370	23.29
1867	56,080,860	6,526,351	23.42	1900	65,190,951	2,397,144	10.43
1873	85,210,319	13,970,243	58.24	1901	56,872,592	2,549,147	10.40
1874	101,371,178	6,104,729	35.11	1902	98,596,473	3,342,473	11.66
1875	128,112,022	9,028,775	48.88	1903	86,512,179	3,324,554	
1876	130,547,168	6,773,177	49.91	1904	88,281,892	3,092,734	
1877	122,994,279	8,309,585	53.77	1905	110,030,285	5,073,233	
1878	122,023,223	7,496,824	47.34	1906	131,281,077	4,554,092	
1879	131,859,429	6,846,510	41.21	1907	129,723,495	4,195,671	
1880	181,190,277	10,265,788	48.65	1908	146,778,080	5,703,641	
1881	208,805,946	11,035,833	50.47	1909	131,153,472	5,608,287	
1882	150,422,377	7,972,780	43.22				

[a] El Archipielago Filipino (1900), **1**, 278.

The above table shows a recent decline in the volume of export that is the result of many causes, both internal and external. One of these may undoubtedly be found in the decreasing fer-

[1] Graduating thesis No. 1.

tility of the cane fields naturally resulting from long-continued planting without replacing the food elements by fertilizer. This phase of the agricultural problem is considered briefly in the following résumé of experiments carried out during 1910 at the College of Agriculture, near Los Baños, Laguna Province, Luzon.

The object of the investigation was to settle the various questions enumerated below:

1. The effect of prolonged soaking on the cane seed.
2. The effect of late planting.
3. The results obtained by various methods of planting.
4. The influence of various fertilizers on the cane as manifested by: (*a*) suckering; (*b*) growth of cane in length; (*c*) growth of cane in circumference; (*d*) production of leaves; (*e*) color of foliage, and (*f*) yield of stripped cane per hectare.

The purple variety of cane was employed throughout, as it appears to be superior to the white.

The experimental plots were located on an old sugar plantation formerly belonging to Mr. Agripino Salva Cruz. The soil was a sandy clay loam with surface layer about 25 centimeters deep and clay subsoil. The field was never artificially fertilized, but had been in continuous use for fifteen years as a sugar hacienda. The land was allowed to lie fallow during the year preceding the experiments, and planted with purple cane in the early part of June, 1910. The tops used for planting were obtained from Negros a month previous, and immediately placed in running water. Thus the period of soaking was excessive, and the date of planting very late.

The field was then divided into 6 plots designated as V–A, V–B, VI–A, VI–B, VII–A, VII–B. Plots V–A, VI–A, and VII–A were unfertilized and served as checks on the 3 corresponding fertilized plots designated as B. The rows of all corresponding plots were continuous from one to the other.

The remaining seed tops were planted in 4 plots, I, II, III, and IV. All tops were about 30 centimeters long, and bore approximately 6 buds each. The fertilizers used consisted of dried blood and compound fertilizer of ammonium sulphate, potassium sulphate, and superphosphate of lime in the proportions of 2 : 3 : 5.[2] Data regarding the amounts of these fertilizers may be found in the subsequent tables.

Ten plants in each plot were selected from continuous stools in rows of average condition, and carefully labeled. Weekly obser-

[2] This fertilizer was furnished gratis by Messrs. Behn, Meyer & Co., Ltd., of Manila.

vations of these plants were made, and the growth of stalk from the base to the longest leaf, as well as the stalk circumference, were carefully noted. The cane from each plot was weighed on April 21, 1911, and the yield calculated.

The data obtained in the plots where different methods of planting were followed are shown in Table II.

TABLE II.—*Results obtained with various distances between rows of cane.*

Plot No.	Plot dimensions.	Distance between rows.	Distance between ends of seed cane.	Tops per hectare.
	Meters.	*Meters.*	*Meters.*	
I_____	40 by 15.75	1.75	0.75	7,125
II_____	40 by 14	1.75	1.00	4,399
III (V-A, VI-A) _____	a 2,378	1.20	.50	10,416
IV _____	40 by 13.2	1.20	.00	27,776
VII-A _____	33.3 by 30	1.20	.33	13,778

a Square meters.

The average growth and condition of the cane in these plots are shown in Table III.

TABLE III.—*Average growth and condition of the cane in the experimental plots.*

Plot No.	Growth in length per week from Aug. 30, 1910, to Apr. 20, 1911.	Length from base to longest leaf on Apr. 20, 1911.	Circumference on Apr. 20, 1911.	Production of leaves per week from Sept. 10, 1910, to Apr. 20, 1911.	Per cent of harvestable suckers to originals.	Harvestable suckers per hectare. a	Originals. b	Yield of stripped cane per hectare.
	Meter.	*Meters.*	*Meter.*					*Kilos.*
I_____	0.0406	2.3775	0.0815	0.939	73	31,198	42,750	143.8
II_____	.0391	2.2121	.0820	.996	81	21,379	26,394	160.8
III (V-A, VI-A)	.0435	2.4595	.0848	.910	70	43,565	62,496	212.1 / 240.8 / 287.4
IV _____	.0444	2.5417	.0800	.894	0	0	166,656	216.8
VII-A _____	.0416	2.3094	.0810	.875	55	45,467	82,668	280.4

a The number of suckers was calculated by subtracting 6—the number of original buds—from the total number of harvestable canes in a stool.

b The number of originals was calculated by multiplying 6—the number of original buds—by the number of seed tops used.

In general, the rate of growth in length was greatest in the most thickly planted plots, while the reverse was true in the gain measured by circumference. The per cent of harvestable suckers was proportionally greater in the thinly planted areas, while the total yields of cane varied irregularly as may be seen from the table.

EXPERIMENTS WITH FERTILIZER

Data regarding the corresponding plots on which fertilizer was used are given in Tables IV, V, and VI.

TABLE IV.—*Data showing the planting followed in fertilized plots.*

Plot No.	Plot dimensions.	Distance between rows.	Distance between ends of seed cane.	Tops per hectare.
	Meters.	*Meters.*	*Meter.*	
V–A	33.3 by 30	1.20	0.50	10,416
V–B	33.3 by 30	1.20	.50	10,416
VI–A	28.3 by 30	1.20	.50	10,416
VI–B	33.3 by 30	1.20	.50	10,416
VII–A		1.20	.33	13,778
VII–B	33.3 by 30	1.20	.33	13,778

TABLE V.—*Data showing the fertilizer used on these plots.*

Plot No.	Ammonium sulphate per hectare.	Potassium sulphate (90 per cent) per hectare.	Calcium super-phosphate per hectare.	Dried blood per hectare.	Cost per hectare.
	Kilos.	*Kilos.*	*Kilos.*	*Kilos.*	*Pesos.*
V–A					
V–B	80	120	200		44
VI–A					
VI–B	80	120	200	150	62
VII–A					
VII–B	40	60	100		22

TABLE VI.—*Average condition of cane in these plots.*

Plot No.	Growth in length per week from Aug. 30, 1910, to Apr. 20, 1911.	Length from base to longest leaf on Apr. 20, 1911.	Circumference on Apr. 20, 1911.	Production of leaves per week from Sept. 13, 1910, to Apr. 20, 1911.	Per cent of harvestable suckers to originals.	Harvestable sucker per hectare.	Originals per hectare.	Yield of stripped cane per hectare.
	Meter.	*Meters.*	*Meter.*					*Kilos.*
V–A	0.0495	2.6810	0.0878	0.900	88	54,996	62,496	240.8
V–B	.0566	2.9621	.0828	.849	111	69,370	62,496	332.6
VI–A	.0385	2.2284	.0848	.932	71	44,452	62,496	287.4
VI–B	.0576	2.8008	.0960	.948	93	58,121	62,496	(?)
VII–A	.0416	2.3054	.0810	.875	55	45,467	82,668	280.4
VII–B	.0592	2.9262	.0816	.939	106	87,628	82,668	350.5

The data for unfertilized plots V–A, VI–A, and VII–A are included in Table VI for comparison with the corresponding fertilized plots V–B, VI–B, and VII–B.

In every case the fertilized plots showed a higher rate of growth in length and a marked tendency toward heavier stalks with more abundant leaf production. The per cent of harvestable suckers was also increased by fertilization. All of these factors combined to increase the yield of stripped cane. Plot VI–B that received the most fertilizer thus showed a yield of cane 79 per cent greater than the corresponding check plot VI–A. The gain in all cases was proportionate to the amount of fertilizer used.

The rate of growth shown by sugar cane in the Philippines is rapid during ten months following planting, reaching a maximum during the third and fourth months. The weekly rates of growth of the various plots are shown in Table VII.

TABLE VII.—*Average weekly growth in length of cane in experimental plots.*

From—	To—	Plot I.	Plot II.	Plot III.	Plot IV.	Plot V-A.	Plot V-B.	Plot VI-A.	Plot VI-B.	Plot VII-A.	Plot VII-B.
		Meter.	*Meter.*	*Meter.*	*Meter.*	*Meter.*	*Meter.*	*Meter.*	*Meter.*	*Meter.*	*Meter.*
Aug. 30	Sept. 6	0.1123	0.1075	0.1151	0.0883	0.0764	0.1108	0.1024	0.1225	0.0690	0.1004
Sept. 6	Sept. 13	.1551	.1251	.1351	.0950	.1633	.1283	.1051	.1938	.1263	.1780
Sept. 13	Sept. 20	.1061	.1231	.1153	.1365	.1348	.1307	.1370	.1468	.1106	.0991
Sept. 20	Sept. 27	.0783	.0693	.0862	.0690	.1266	.0859	.0901	.1386	.1190	.1287
Sept. 27	Oct. 4	.0478	.0434	.0926	.0820	.0950	.0831	.1064	.1185	.0874	.0892
Oct. 4	Oct. 11	.1296	.0735	.1124	.0889	.1017	.1440	.1400	.1349	.1151	.1039
Oct. 11	Oct. 18	.0676	.0651	.0658	.0780	.1111	.1411	.0682	.1260	.1403	.1029
Oct. 18	Oct. 25	.0311	.0382	.0479	.0566	.0561	.0940	.0441	.0788	.0509	.0914
Oct. 25	Nov. 1	.0335	.0410	.0489	.0587	.0595	.0960	.0422	.0736	.0680	.0929
Nov. 1	Nov. 8	.0413	.0453	.0564	.0668	.1050	.1050	.0544	.0824	.0673	.1093
Nov. 8	Nov. 15	.0451	.0488	.0428	.0478	.0743	.0852	.0441	.0693	.0441	.0762
Nov. 15	Nov. 22	.0529	.0577	.0407	.0394	.0732	.0733	.0414	.0578	.0383	.0721
Nov. 22	Nov. 29	.0544	.0562	.0395	.0417	.0703	.0633	.0378	.0497	.0332	.0627
Nov. 29	Dec. 6	.0632	.0587	.0409	.0500	.0704	.0690	.0352	.0520	.0313	.0613
Dec. 6	Dec. 13	.0332	.0364	.0310	.0440	.0587	.0577	.0277	.0427	.0330	.0565
Dec. 13	Dec. 20	.0267	.0324	.0297	.0405	.0557	.0613	.0248	.0412	.0315	.0608
Dec. 20	Dec. 27	.0297	.0280	.0273	.0434	.0518	.0608	.0232	.0381	.0280	.0569
Dec. 27	Jan. 3	.0258	.0325	.0299	.0418	.0522	.0539	.0256	.0371	.0254	.0581
Jan. 3	Jan. 10	.0244	.0312	.0287	.0462	.0506	.0443	.0223	.0371	.0285	.0482
Jan. 10	Jan. 17	.0201	.0290	.0352	.0352	.0094	.0378	.0098	.0373	.0161	.0430
Jan. 17	Jan. 24	.0197	.0254	.0294	.0348	.0092	.0302	.0082	.0358	.0142	.0372
Jan. 24	Jan. 31	.0171	.0215	.0276	.0320	.0063	.0262	.0086	.0297	.0108	.0359
Jan. 31	Feb. 7	.0106	.0179	.0248	.0469	.0033	.0230	.0024	.0233	.0107	.0347
Feb. 7	Feb. 14	.0168	.0213	.0235	.0248	.0141	.0173	.0205	.0298	.0166	.0303
Feb. 14	Feb. 21	.0191	.0178	.0209	.0219	.0138	.0133	.0150	.0254	.0153	.0282
Feb. 27	Feb. 28	.0175	.0165	.0169	.0183	.0094	.0121	.0128	.0214	.0109	.0224
Feb. 28	Mar. 7	.0163	.0131	.0155	.0170	.0093	.0116	.0099	.0193	.0105	.0158
Mar. 7	Mar. 14	.0137	.0086	.0106	.0222	.0112	.0085	.0075	.0182	.0128	.0173
Weekly average to Apr. 20 ----------		.0082	.0038	.0056	.0068	.0031	.0034	.0030	.0066	.0040	.0116

The fertilizer should evidently be applied before the period of maximum growth to be most effective.

SUMMARY

The cane grew well in spite of late planting and long soaking of the seed. The per cent of harvestable suckers varied from 0, where the cane was thickest, to 81 in the plot where the plants were farthest apart. These low figures are doubtless due to late planting, as neighboring estates where cane is grown with even less space between the tops often produce from 200 to 300 per cent of suckers.

The sugar content of original plants has been shown [3] to exceed that of the suckers, and a correct balance between originals and suckers will give, therefore, a maximum sugar output per hectare.

The use of fertilizer was very beneficial on the soils used in these experiments, and increased the yield of stripped cane to a marked extent. Many fields are in a similar exhausted state so far as sugar cane is concerned, and would doubtless give corresponding returns for capital spent in suitable fertilizer.

The results obtained in the preceding experiments clearly show the necessity of artificially replacing the food elements which long-continued planting has removed from many sugar haciendas, and indicate the increased output that may be expected from such treatment.

[5] Stubbs, William C., Sugar Cane. Issued by the State Bureau of Agriculture and Immigration. [Louisiana. No date] (1897 ?), 1, 105.

THE TWO PHTHALOXIMES: A STUDY OF THEIR ABSORPTION SPECTRA AND CONSTITUTION

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Two plates and 6 text figures

Phthaloxime was first described by Lassar-Cohn,[2] who made it by the action of phthalyl chloride on hydroxylamine. The same compound was later made by Lach,[3] who employed phthalic anhydride and hydroxylamine. Orndorff and Pratt [4] have shown that the course of this reaction depends upon the temperature.

A colorless phthaloxime is formed at 60°, and a lemon yellow isomer results when the same reaction takes place at 100°. These two isomers are very closely related, as shown by their physical characteristics and chemical properties. The principal difference between them is their color. Two structures are theoretically possible for phthaloxime, depending upon whether the hydroxylamine residue is in the symmetrical (1), or unsymmetrical (2), position in respect to the benzene ring.

1.   2.
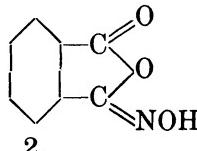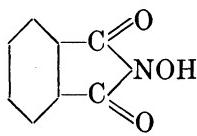
The symmetrical formula (1) has been generally assigned to colorless oximes of this type regardless of the color of their salts. Both the white and the yellow phthaloxime give alkali salts of a brilliant red and of almost identical color in both cases. It has not been found possible, as yet, to prove beyond question which of the above formulas should be applied to phthaloxime, although a careful study of its formation and reactions points

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[2] *Ann. d. Chem.* (Liebig) (1880), **205**, 295.
[3] *Ber. d. deutschen chem. Ges.* (1893), **16**, 1781.
[4] *Am. Chem. Journ.* (1912), **47**, 89.

strongly to the unsymmetrical structure. The fact that phthaloxime may be made from phthalyl chloride and hydroxylamine does not distinguish between the two structures, as the reaction is not a mere elimination of hydrogen chloride with the formation of the oxime, but takes place in two steps, giving phthalhydroxamic acid as an intermediate product. Ott [5] has recently shown that the ordinary phthalyl chloride may be symmetrical, a fact indicated by its absorption spectrum according to Scheiber.[6] It is evident that an unsymmetrical oxime may result from a symmetrical chloride in the following manner:

$$\text{[ring]} \begin{matrix} -CO\ Cl \\ -CO\ Cl \end{matrix} \quad +NH_2OH \rightarrow \quad \text{[ring]} \begin{matrix} -C\!\!\begin{smallmatrix} Cl \\ OH \\ NHOH \end{smallmatrix} \\ -CO\ Cl \end{matrix}$$

Phthalyl chloride.

$$\text{[ring]} \begin{matrix} -C\!\!\begin{smallmatrix} Cl \\ OH \\ NHOH \end{smallmatrix} \\ -CO\ Cl \end{matrix} +2H_2O \rightarrow \quad \text{[ring]} \begin{matrix} -C\!\!\begin{smallmatrix} NHOH \\ =O \end{smallmatrix} \\ -C\!\!-OH \\ \quad\ \ \backslash\!\!\!\diagdown O \end{matrix} +2HCl$$

Phthalhydroxamic acid.

$$\text{[ring]} \begin{matrix} -C\!\!\begin{smallmatrix} NHOH \\ =O \end{smallmatrix} \\ -C\!\!\begin{smallmatrix} OH \\ \diagdown O \end{smallmatrix} \end{matrix} \rightarrow \quad \text{[ring]} \begin{matrix} -C=NOH \\ \quad\quad >O \\ -C\!\!\begin{smallmatrix} \\ \diagdown O \end{smallmatrix} \end{matrix} +H_2O$$
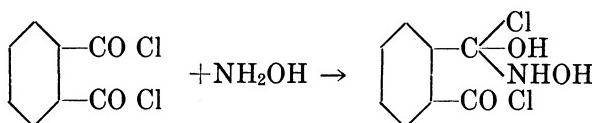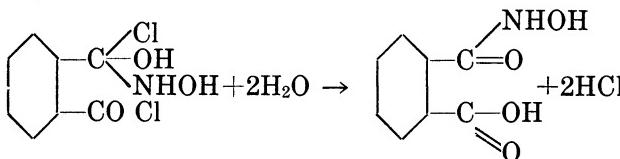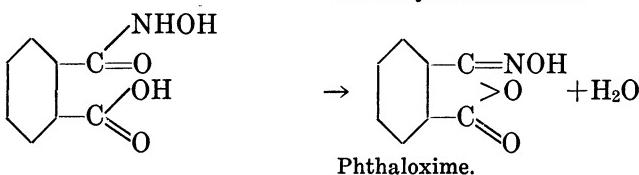
Phthaloxime.

The reactions are entirely analogous to these between phthalyl chloride and ammonia.[7] Phthalhydroxamic acid cannot be isolated from solution as it loses water to form the oxime, but its presence may be shown by the characteristic color given with ferric chloride, and its alkali salts may be obtained as colorless crystals. The reaction between phthalic anhydride and hydroxylamine follows a similar course. The anhydride combines with the free hydroxylamine giving a *clear solution* of hydroxamic acid. Since both the anhydride and the oxime are very slightly soluble in water, it is evident that the first phase of the reaction may be completed before dehydration with the result-

[5] *Ann. d. Chem.* (Liebig) (1912), **392**, 245.

[6] *Ibid.* (1912), **389**, 121.

[7] Scheiber, *Ber. d. deutschen chem. Ges.* (1912), **45**, 2252.

ing formation of oxime takes place.   Further heating of the solution causes an abundant crystallization of phthaloxime.

When phenylhydrazine acts similarly with phthalic anhydride, the product of the first phase may be isolated.   Anilidophthalamic acid is formed in this case,[8] and has a structure analogous to phthalhydroxamic acid.

$$\left[\text{benzene ring}\right]\begin{array}{l} -C{\overset{\nearrow O}{\underset{}{}}}-OH \\ -C-NH\cdot NHC_6H_5 \\ {\searrow O} \end{array}$$
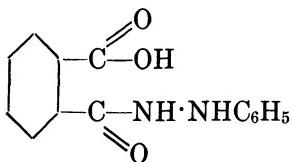
<div align="center">Anilidophthalamic acid.</div>

Phthaloxime may also be made by the action of hydroxylamine on phthalimide in alkaline solution.   Here again the formation of an intermediate product precludes any conclusions being drawn regarding the position of the =NOH group, although phthalimide possesses a symmetrical structure.   The reaction is represented by the following equation:

$$\left[\text{ring}\right]\begin{array}{l}-C{\overset{\nearrow O}{}} \\ {\diagdown}NH \\ -C{\diagup} \\ {\searrow O}\end{array}+NH_2OH+H_2O \;\rightarrow\; \left[\text{ring}\right]\begin{array}{l}-C{\overset{\nearrow O}{}}-OH \\ -C-NHOH \\ {\searrow O}\end{array}+NH_3$$
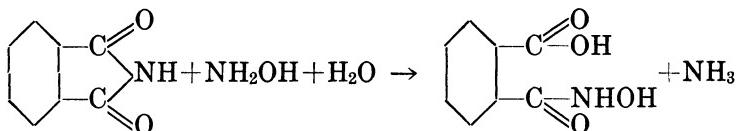
Ammonia is liberated and phthalhydroxamic acid formed.   This may be converted into either the white or yellow phthaloxime according to the temperature at which the solution is heated after being acidified.

The existence of two isomeric phthaloximes may be explained by means of the unsymmetrical formula in a manner similar to that employed with the benzaldoximes, and indicated graphically by the formulas IIa and IIb where the *syn* type shows the hydroxyl in closer proximity to the unsaturated carbonyl group.

$$C_6H_4\begin{array}{c} C=O \\ \diagup \quad \diagdown \\ \quad O \\ \diagdown \quad \diagup \\ C \\ \| \\ N-OH \end{array} \qquad\qquad C_6H_4\begin{array}{c} C=O \\ \diagup \quad \diagdown \\ \quad O \\ \diagdown \quad \diagup \\ C \\ \| \\ HO-N \end{array}$$
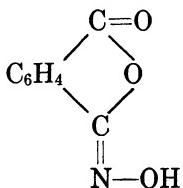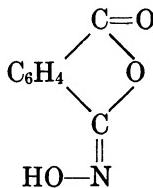
<div align="center">IIa Syn.   IIb Anti.</div>

[8] Hötte, *Journ. f. prakt. Chem.* (1887), II, **35**, 268.

A study of the absorption spectra of these and related compounds was undertaken for the purpose of obtaining an insight into their molecular arrangement and behavior and evidence regarding the production of color in their salts.

If the isomerism between the white and yellow phthaloximes is correctly indicated by the above formulas, IIa and IIb, it is evident that their absorption spectra must be very closely related. Macbeth, Stewart, and Wright [9] have studied the action of light on unsaturated centers in a molecule, and state that no great change takes place in the general absorptive power of a molecule when such a center is shifted in space with respect to a saturated radical. The carbonyl group in phthaloxime represents the point of maximum unsaturation, while the hydroxyl can hardly be looked upon as the center of much residual affinity. Any relative change in space between carbonyl and hydroxyl should produce a slight modification in the absorption spectrum, but the type would remain the same. Hartley [10] has shown that the stereoisomeric benzaldoximes have the same absorption spectra which show a broad band in the benzene region.

Hantzsch [11] has examined several isomeric oximes and states that the absorption spectra of α and γ benzyl oximes, the two para nitrobenzaldoximes, and of the chlortoluquinonoximes show great similarity in each case between the two isomers. The *syn* series absorbs somewhat more strongly than the *anti,* as might be expected from the greater proximity and consequent mutual influence of the two radicals. Wilson and Heilbron [12] have recently prepared two semicarbazones of mesityl oxide, and find corresponding differences due to nitrogen stereoisomerism. Since these characteristics are manifested in the case under discussion, it thus appears that the yellow phthaloxime should be designated as *syn*-phthaloxime and the white isomer as *anti*-phthaloxime as represented by formulas IIa and IIb.

Prior workers have pointed out that absorption bands are not to be attributed to any definite molecular structure, but rather to the existence of dynamic compounds which are not necessarily capable of isolation. The presence of an absorption band is due to intramolecular change from one modification to another, and is expressed by an actual change of linking, or is due to the po-

[9] *Journ. Chem. Soc. London* (1912), **101,** 599.

[10] *Ibid.* (1900), **77,** 509.

[11] *Ber. d. deutschen chem. Ges.* (1910), **43,** 1651.

[12] *Journ. Chem. Soc. London* (1913), **103,** 377.

tential possibility of such a change. The oscillation or **free period** in connection with the reversible transformation of one tautomeric form into another is synchronous with the oscillation of the light waves absorbed. This transformation must be understood to include changes that cannot be graphically represented by fixed structural formulas. These peculiar cases are best indicated according to the partial valency theory developed by Thiele.[13] This assumes that all the affinity of two atoms connected by a double bond is not used in holding the atoms together, but that there is a slight excess present in each atom. Thiele designates this excess affinity by dotted lines. Application of this idea to phthaloxime gives a formula that may be expressed thus:

$$C_6H_4 \diagdown \begin{array}{c} C = O \\ > O \\ C = NOH \end{array}$$
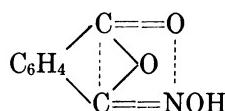
The two sets of partial valencies may be assumed more completely to neutralize each other during one phase of the benzene vibration when the atoms are in closer proximity to each other than during the succeeding phase when they are more widely separated. This varying adjustment of forces in connection with the disturbing influence of the hydroxyl group may be thought of as causing the ultra-violet absorption band of phthaloxime. The equilibrium is essentially the same in phthalic acid, the esters of phthalic acid, and very similar in phthalimide. All of these compounds may be expressed by analogous formulas. Moreover, they all give absorption spectra showing similar ultra-violet absorption bands. This must be considered as evidence of corresponding structure. The influence of the benzene ring is essential in these cases.

The application of the partial valency theory to explain the activity of carbonyl groups removes the indefiniteness inherent in the method employed by Stewart and Baly [14] to represent this condition. These authors suggest that nascent carbonyl groups be indicated by printing the oxygen in heavy-faced type, thus

$$-\overset{|}{\underset{O}{C}}-,$$

and that this condition is essentially dynamic in nature and cannot be successfully represented by structural formulas which

[13] *Ann. d. Chem.* (Liebig) (1899), **306**, 87.
[14] *Journ. Chem. Soc. London* (1906), **89**, 497.

are static in their meaning. The term *isorropesis* was proposed to designate the interrelation between groups of this type. The activity of a carbonyl radical is not inherent in the group itself, but is produced by the action of neighboring atoms that render the group nascent.[15] The causes underlying this action are more easily understood by means of the partial valency theory. The amount of affinity in excess of that utilized in holding the doubly bound atoms together will depend upon the presence of free affinity exerted by neighboring atoms. In the absence of such forces, the energy of the two atoms will be mutually neutralized and in equilibrium.

When phthaloxime is converted into its salts, a marked altera-tion in molecular vibration is manifested to the eye by the change from a colorless compound to a colored one. The new vibration may be due either to a different equilibrium of the same molecule induced by the presence of a positive metal atom, or to an actual alteration in molecular structure.

COLOR DUE TO CHANGE IN EQUILIBRIUM BETWEEN PARTIAL
VALENCIES

If the production of color in the formation of salts of phthal-oxime is due to a change in the vibration of the molecule un-accompanied by atomic tautomerism, it must be dependent upon a new equilibrium between the partial valencies of the unsatu-rated groups. The change of equilibrium is not to be attributed to the increased weight of the molecule and consequent reduc-tion in the period of vibration. The replacement of the acidic hydrogen by groups with high molecular weight, as in the case of the benzoate, causes a change in the activity of the molecule shown by a reduction in the persistence of the characteristic absorption band in the spectrum. However, the type of spectrum remains the same. Therefore, the activity of the hydrogen is not greatly different from that of various organic radicals, and the compound retains its true oxime condition in every case. It is to be noted that an aqueous solution of oxime shows a slightly more pronounced yellow tint than a correspond-ing alcohol solution and that the color in both cases is decreased by a trace of mineral acid. The ethers and esters of the oxime do not behave in an analogous manner, but always give solutions of equal color intensity that are unchanged by traces of acid. The acidic hydrogen, therefore, influences the equilibrium to a

[15] Baly and Schaefer, *ibid.* (1908), **93**, 1814.

slight extent depending upon the solvent, although the activity is not sufficient to cause any indication of a color band in the absorption spectrum.   The stronger general absorption of the oxime as compared with the benzoate shows a tendency toward the production of a band, as might be expected.

The replacement of hydrogen by a metal atom introduces a strong positive sphere of influence that must have a greater disturbing effect on the negative latent valencies.   The more positive the metal or group introduced, the greater will be the resulting change produced.   The following table of optical properties of phthaloxime and various derivatives shows that the character of light transmitted by the crystals may be arranged in a graded scale corresponding with the increasing basicity of the substituting atom or radical.

TABLE I.[a]—*Optical properties of phthaloxime and derivatives.*

Compound.	Character of light rays transmitted through crystals.	Degree of pleochroism.
White oxime	White	Absent.
Ethyl ether of yellow oxime	White and faint greenish yellow	Faint.
Yellow oxime	White and yellow	Do.
Acid sodium salt of white oxime	Pale yellow and orange	Marked.
Ammonium salt of white oxime	Straw yellow and reddish orange	Strong.
Sodium salt of white oxime	Pale purple and deeper purple	Rather marked.

[a] Determinations made by Professor Gill, mineralogical department, Cornell University; see Orndorff and Pratt, *loc. cit.*

The potassium salt forms very small crystals that are difficult to examine, but in bulk the color appears darker than the corresponding sodium salt.   The differences existing among the above salts in crystalline condition are very distinct, but cannot be accurately shown spectroscopically.   Alcohol solutions of the ammonium, lithium, barium, sodium, and potassium salts were photographed.   All of these solutions in hundredth molar concentration showed a well-marked color absorption band increasing in width and persistence in the order named.   This was partly due to the different dissociation constants of the various alkalies, but this factor could not be eliminated in as much as the addition of an excess great enough to compensate for the dissociation always resulted in the formation of hydroxamic acid and destruction of the oxime.

A very weak base such as pyridine dissolves phthaloxime with slight change of color, and the solution gives an absorption spectrum showing no band in the visible region.   This indicates that

if a salt is formed it must have the true oxime structure. The addition of increasing amounts of water to the pyridine solution causes a progressive deepening of color and gradual production of a color band until the characteristic red of the alkali salts is obtained. This effect is explained by the increased basicity of the pyridine hydrate formed upon the addition of water. The salt is unstable, and could not be isolated from solution without the entire loss of pyridine.

The silver salt of phthaloxime is insoluble in the ordinary solvents, and its true absorption spectrum could not be obtained. It dissolves readily in pyridine with a purplish red color, probably due to the formation of an addition product containing the strongly positive silver dipyridine. A similar product was isolated in the case of ammonia where one molecule of crystalline silver salt was combined with one molecule of ammonia. These addition products are deeply colored as might be expected from the strength of the double base. That the absorption band of their spectra heads at a different place than that characteristic of the alkali oxime salts is probably due to the presence of additional latent valencies in the unsaturated nitrogen atom of the pyridine-silver or ammonia-silver groups.

It is evident that the introduction of various positive atoms or radicals into the phthaloxime molecule may cause different changes in its optical activity. It may be assumed that the previous condition of equilibrium existing between the unsaturated $=CO$ and $=NOH$ groups is completely changed, and that the latent valencies of these groups no longer mutually neutralize each other, but that a negative portion swings to the positive metal. The equilibrium will be slightly different in various salts depending upon the electropositiveness of the substituting atom or group, but will always be of the same type unless further complicated by the introduction of other unsaturated atoms. The result of the new equilibrium between the positive group or atom and the negative partial valency of an unsaturated atom is shown by the disappearance to a greater or less extent of the absorption spectrum characteristic of the original type and the production of a new band in the spectrum.

The position of the new band and consequent color, in the broad sense, of the salt given by any compound undergoing changes of this general type will depend upon the resulting configuration of the molecule. The presence of the benzene ring or its equivalent in the molecule is probably essential whenever the absorption band of the salt falls in the characteristic quinone position.

The molecular equilibrium of phthaloxime salts may be represented by the formula:

$$C_6H_4 \underset{C=NO}{\overset{C=O\cdots}{\diamondsuit}} \!\!O \quad M$$
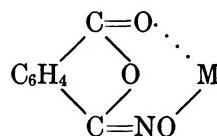
This indicates merely the partial valency equilibrium between negative carbonyl and positive metal, and shows a ring formation resembling the quinoid configuration. It is to be noted that neither phthalic acid nor phthalimide can give analogous salts, although the compounds themselves present a condition similar to that of the oxime. The addition of alkali to solutions of these substances causes no radical change in the position of their absorption bands, but causes a marked increase in the width of the original band of the latter, indicating a difference in degree of the existing equilibrium rather than a change in character.

The application of the partial valency theory to colored salts has been utilized by Werner [16] in the case of the yellow benziloxime. He gives these compounds the following structure:

$$C_6H_5-\underset{\underset{\diagdown}{N}}{\overset{|}{C}}\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!C\!-\!C_6H_5 ,$$

$$\diagdown O-M \cdots$$
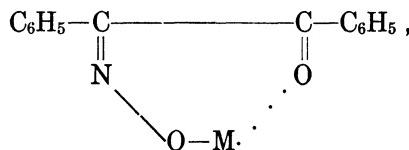
but makes no mention of the equilibrium that must exist between the unsaturated groups before the entrance of the metal atom. Hantzsch has also used similar conceptions in much of his later work, and has applied partial valency structures to many compounds in which it is otherwise very difficult to explain the absorption spectra.

Lassar-Cohn calls attention to the resemblance between phthaloxime and the nitrolic acids, and Hantzsch and Kanasirski [17] have studied the absorption spectrum of the latter. They find that ethyl nitrolic acid,

$$H_3C-C\!\!\underset{\diagdown NOH,}{\overset{\diagup NO_2}{}}$$
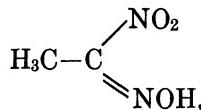
[16] *Ber. d. deutschen chem. Ges.* (1908), **41**, 1062.
[17] *Ibid.* (1909), **42**, 889.

shows only general absorption, while its red potassium salt gives a broad absorption band heading at $\frac{1}{\lambda} = 3050$.

In this case there is no possibility for quinoid formation in a ring in connection with conjugated linking between unsaturated groups, and the colored salts do not give absorption spectra showing a band in the quinone region. There is, however, a marked difference between the spectra of the salts and free acid. Hantzsch represents the equilibrium of the former by the formula:

$$H_3C-C\begin{array}{c} \diagup NO_2 \\ \diagdown NO \end{array}\Bigg\} M$$
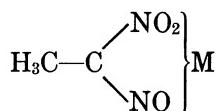
This explains the change in optical properties that takes place when the acid is converted into its salts, and corresponds to our oxime structure.

Certain diketones represented by the type of indandions are colorless or very faintly yellow, but dissolve in alkaline solutions giving highly colored salts. In this case the salt formation has been shown to take place with a tautomeric change from the keto to the enol form as represented by the formulas:

$$C_6H_4\begin{array}{c} \diagup C=O \\ \diagdown C=O \end{array}CHR \rightarrow \qquad C_6H_4\begin{array}{c} \diagup C=O \\ \diagdown C-OH(M) \end{array}CR$$
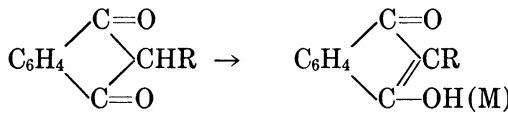
Keto indandion.   Enol indandion.

The alkali salt exists in the conjugated form according to Hantzsch [18] who represents this condition as

$$C_6H_4\begin{array}{c} \diagup C====O\cdot \\ \diagdown C----O \end{array}CR \quad M$$
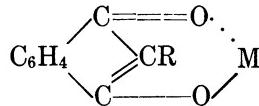
Conjugated enol salt of indandion.

This class of compounds is evidently more nearly related to the phthaloximes than are the nitrolic acids. There are several important points of difference, however, that serve to throw light

[18] *Ann. d. Chem.* (Liebig) (1912), **392**, 286.

upon the structure of the oximes. The absorption spectra of the indandions have been carefully studied by Hantzsch, and found to vary in a marked degree with change of solvent. Phenyl indandion was shown to give only general absorption in ether solution, but selective absorption in methyl alcohol with 1 well-developed band and 2 step-offs. In the presence of alkali these develop into 3 well-marked absorption bands. The equilibrium of the enol-keto tautomerism in ether solution differs from that in methyl alcohol, and causes a corresponding difference in the absorption spectra.[19]

The application of Hantzsch's work to our problem gives additional evidence concerning the structure of phthaloxime. If the oxime were correctly represented by the symmetrical formula, it might be expected to resemble the indandions both chemically and spectroscopically, and undergo enol-keto tautomerism. The absorption spectra would show this equilibrium, and the approximate amount of the enol form in solution could be determined by titration with bromine.[20] Molecular rearrangement of this type would result in the following equilibrium:

$$C_6H_4 \overset{\diagup C=O}{\underset{\diagdown C=O}{\diagup} NOH} \rightleftarrows C_6H_4 \overset{\diagup C-OH(M)}{\underset{\diagdown C=O}{\diagup} NO}$$
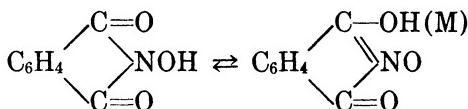
Solutions of phthaloxime do not react with aqueous bromine, however, and no chemical or optical indications of enol-keto tautomerism could be observed. Moreover, the absorption spectra of the oximes in various neutral solvents are practically identical, do not show evidences of an enol-keto band, and are of an entirely different type from those given by the indandions. The other alternative for salt formation with a symmetrical oxime would be direct replacement of hydrogen by a metal atom, giving salts analogous in many respects to the salts of phthalimide. Since neither of the above conditions is characteristic of phthaloxime, it seems very probable from spectroscopic evidence alone that only the unsymmetrical structure will explain the facts.

Oximido-oxazolone is colorless or faintly yellow, and also forms highly colored salts with colorless metals. Hantzsch[21]

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[19] Hantzsch, *loc. cit.*

[20] Meyer, *Ann. d. Chem.* (Liebig) (1911), **380**, 212.

[21] *Ber. d. deutschen Chem. Ges.* (1909), **42**, 1007; (1910), **43**, 68.

represents the chromophoric development in this case by the formulas:

Oximido-oxazolone.   Oximido-oxazolone salts.
(Colorless.)   (Colored.)
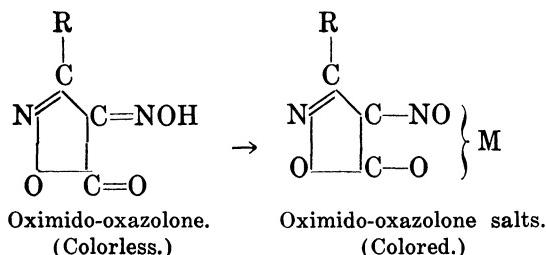
He has found that this oxime shows only general absorption in its spectrum, while solutions of its salts are strongly selective with a well-marked band in the color region. It is evident that conditions in compounds of this type are similar to those in phthaloxime as far as the production of color upon salt formation is concerned. There is no possibility for quinoid configuration of a ring in the oximido-oxazolones, yet the change in their absorption spectra upon the addition of alkali closely resembles that shown by phthaloxime. It does not seem essential, therefore, to assume an actual quinoid structure in the latter case, but merely that the two rings act similarly toward the conjugated partial valencies in both classes of compounds, and that the general effect of a positive metal atom in the molecule is analogous.

COLOR DUE TO MOLECULAR REARRANGEMENT

There are several factors which render it improbable that the salts of phthaloxime possess a different molecular structure from that of the oxime. The red silver salt reacts easily and at low temperatures with alkyl iodides giving ethers that undoubtedly possess the true oxime structure. These ethers are colorless in the case of the colorless isomer, and faintly yellow when derived from the yellow oxime. They are broken down by solutions of the caustic alkalies into substituted hydroxylamines, and give absorption spectra closely resembling the parent oximes. No ethers have thus far been made that show the color characteristic of the salts, and if formed as the first phase of the reaction between silver salt and alkyl iodide they must be very unstable.

Since the two phthaloximes have been shown to retain their identity when converted into salts,[22] any formula representing a different arrangement of the molecule to explain color must include the doubly bound nitrogen upon which the isomerism

[22] Orndorff and Pratt, *loc. cit.*

depends.   Two possible formulas representing the oxime salts may be expressed as:

$$C_6H_4 \diagup{C}\diagdown\diagup{OM}\diagdown{O} \quad \text{and} \quad C_6H_4 \diagup{C}\diagdown\diagup{OM}\diagdown{O}\diagdown{C}=N=O,$$
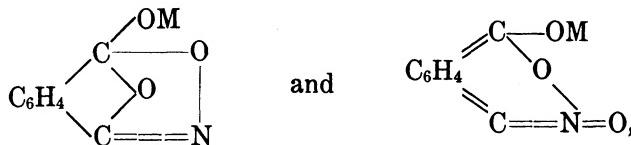
the second of which would explain color formation as depending upon the quinoid condition of the benzene ring and might be considered as in equilibrium with the first.   The theory of partial valency may also be applied to the second formula giving a conjugated linking in the side chain that may be represented by the formula:

$$=\!C\!-\!O \diagdown_{\cdot \cdot}M$$
$$O\!\diagup_{=\!N=\!\!=O\cdot\cdot}$$
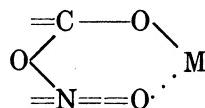
The salts would then belong to the enol-nitroso type.

   No method is available to decide definitely between these two explanations of the very marked change that takes place when phthaloxime is converted into its highly colored salts.   The partial valency theory explaining color as dependent upon a changed condition of equilibrium brought about by a positive metal atom without actual molecular rearrangement has much to recommend it, and seems to be in better accord with our present ideas of chromophoric chemistry.

ABSORPTION SPECTRA OF THE PHTHALOXIMES, THEIR METHYL ETHERS, ACETATES, AND BENZOATES

   The complete curves of the absorption spectra of the two phthaloximes are shown in fig. 1.   Solutions in absolute alcohol were employed when not otherwise stated, and the spectra photographed with a Hilger spectrograph [23] using a nickel arc as the source of light.

   The curves are plotted with logarithms of thickness of layer in millimeters of ten thousandth molar concentration as ordinates, and oscillation frequencies of the limits of transmission as abscissa.
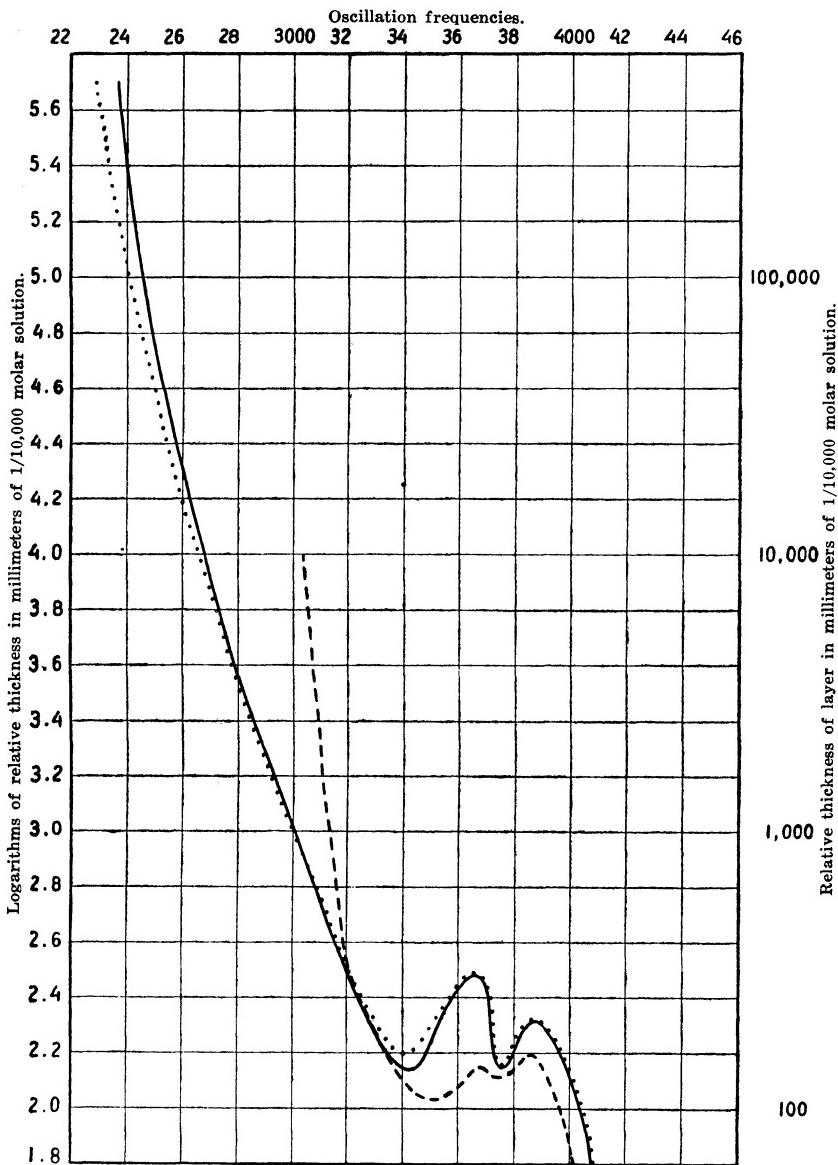
Fig. 1. Full curve = white phthaloxime.
Dot curve = yellow phthaloxime.
Dash curve = benzoate of white phthaloxime.

Description of fig. 1.—The region of greatest difference between the two curves is found in the total absorption at high concentrations. The upper limit of these curves from log. 5.3 to 5.7 represents higher concentrations than can be conveniently

handled with alcohol alone as a solvent. A mixture of equal parts of alcohol and acetone proved satisfactory for this region. The yellow isomer shows greater total absorption in the visible spectrum. With decreasing concentration the curves approach until they are practically identical, but separate again as they reach the absorption band at $\frac{1}{\lambda} = 3400$ where the white isomer shows slightly greater persistence. The benzene bands, numbers 1, 2, 4, and 6, are clearly defined in neutral or acid solution although not separately plotted in fig. 1.

The absorption curve of the benzoate of white phthaloxime is also shown in fig. 1. The spectra of the methyl ethers and acetates were also studied, but are not plotted as the curves fall between the oximes and the benzoates. All of these curves are very similar. The absorption bands extend to about the same dilution for each compound, but the intervening transmitted portion is very different in each case. The transmission band at $\frac{1}{\lambda} = 3676$ decreases from about 2.5 in the oximes and methyl ethers to 2.4 in the acetates and 2.15 in the benzoates. The transmission bands bounding the other benzene absorption bands show about the same decrease; that is, the transmission band heading at $\frac{1}{\lambda} = 3870$ persists to about log. 2.32 in the oximes, 2.25 in the acetates, and 2.20 in the benzoates.

THE METHYL ETHERS OF THE TWO PHTHALOXIMES

The methyl ethers of the two oximes were made by treating the respective silver salts suspended in ether with methyl iodide. The reaction proceeds rapidly at room temperature with the separation of silver iodide. The ethers were extracted from the residue and recrystallized from alcohol in the form of long needles, that of the white oxime being colorless while the corresponding derivative of the yellow oxime is faintly yellow. Both ethers melt at 133° uncorrected.

THE BENZOATES OF THE TWO PHTHALOXIMES

The two benzoates were similarly made from the silver salts and benzoyl chloride. They crystallize from alcohol in columns, one colorless and the other faintly yellow. Both melt at 171°.5 uncorrected. The benzoates may conveniently be prepared also from benzoyl chloride and an alkali salt of the oxime dissolved in water.

THE ALKALI SALTS OF THE TWO PHTHALOXIMES

The profound changes that take place in phthaloxime on the addition of alkali are manifested in the absorption spectra by the appearance of a broad absorption band extending from about $\frac{1}{\lambda} = 1800$ to 2860, and heading at $\frac{1}{\lambda} = 2300$. The absorption band of the oximes heading at $\frac{1}{\lambda} = 3400$ decreases regularly with increasing concentrations of alkali, and practically disappears when the amount of alkali is sufficiently great to effect the complete transformation into the red salt. These differences with various concentrations of alkali are shown in fig. 2.
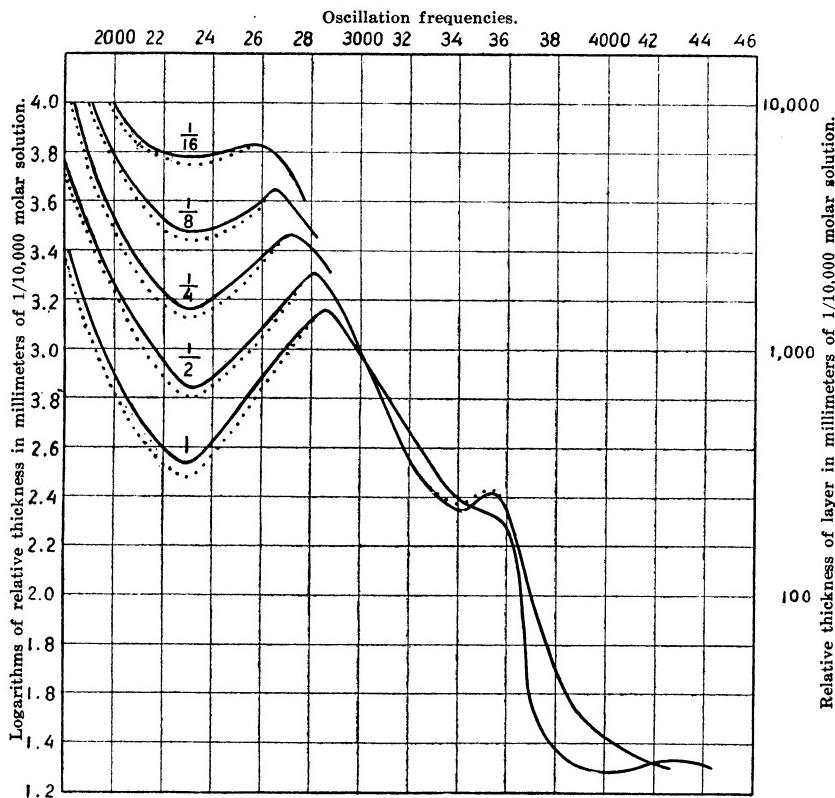
Fig. 2. Full curves = white phthaloxime with 1/16, 1/8, 1/4, 1/2, and 1 equivalent of sodium ethoxide.
        Dot curves = yellow phthaloxime with corresponding alkali.

Description of fig. 2.—In order to avoid confusion arising from the large number of lines, the curves with one-sixteenth, one-eighth, and one-quarter molecular equivalents of alkali are not

drawn throughout the entire regions measured. It is sufficient to state that they lie between the curve of the oxime itself and that formed with one-half equivalent of alkali.

These curves are plotted from photographs made through absolute alcohol solutions wherever possible. Since the desired concentration could not always be obtained with this solvent, 90 per cent alcohol was used when 1 equivalent and one-half equivalent of alkali were employed in the 1/100 molar solutions, and 99 per cent alcohol for the 1/1000 molar solutions. Ninety-five per cent alcohol solutions were used for the other 1/100 molar concentrations. These small amounts of water have no appreciable effect upon the curves.

The difference between the yellow and the white modification of the oxime is here manifested in the color absorption band. This has a greater persistence in the yellow than in the white, and shows that the salts of the former are somewhat more deeply colored than the corresponding salts of the latter.
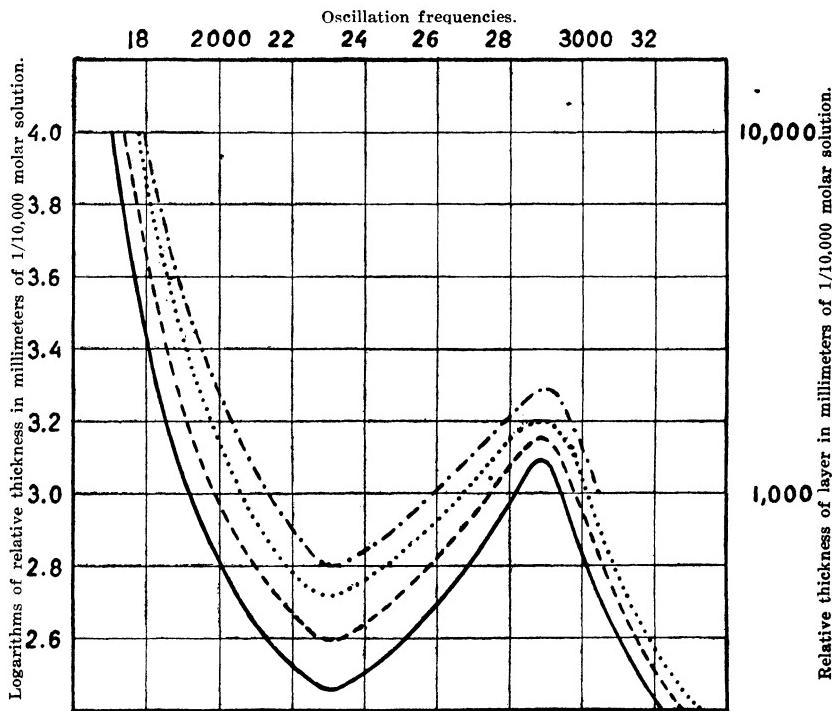
Fig. 3. Salts of white phthaloxime in 90 per cent alcohol.
Full curve = potassium salt.
Dash curve = sodium salt.
Dot curve = barium salt.
Dash and dot curve = ammonium salt.

THE ABSORPTION SPECTRA OF PHTHALOXIME SALTS IN 90 PER CENT
ALCOHOL

Weighed quantities of the pure salts were dissolved in the requisite volume of water and absolute alcohol added at once to make a 90 per cent alcohol solvent. In this manner exactly 1 equivalent of alkali to 1 of oxime was easily obtained. Photographs were made on Cramer's spectrum plates to cover as much of the color absorption band as possible, and the curves in fig. 3 plotted from these.

Description of fig. 3.—The curves show that the ammonium, barium, sodium, and potassium salts give absorption bands heading at $\frac{1}{\lambda} = 2300$ in each case, but appearing at increasing dilutions. The original ultra-violet oxime band heading at $\frac{1}{\lambda} = 3400$ was most pronounced in the ammonium salt and least in the potassium. The barium and sodium salts give intermediate curves. The residual oxime band gives an indication of the relative dissociation of the different salts, and corresponds in persistence inversely with the strength of the base. The silver salt of phthaloxime in crystalline form shows a deeper red than the corresponding potassium salt, but could not be included in the series because of its insolubility.

THE ABSORPTION SPECTRA OF PHTHALOXIME AND ITS SALTS IN
PYRIDINE

Pyridine is the only suitable solvent for the silver salt, and gives a deep purplish red solution containing an addition product of salt and base.

Description of fig. 4.—The absorption band appears at greater dilution, and heads at $\frac{1}{\lambda} = 2140$. It is of the same general type as the corresponding band given by the alkali salts, but shows by its position farther toward the red that a slightly different molecular equilibrium is represented in the compound. The curve given by oxime in pyridine shows general absorption extending into the visible spectrum, but retaining the oxime type. It is probable that no true salt is formed since a weighed amount of oxime did not gain in weight when dry pyridine vapor was passed over it. The dash curve represents oxime dissolved in a mixture containing equal volumes of water and pyridine. The color of this solution is deep red, and the absorption spectrum clearly shows the presence of a true salt.

THE ABSORPTION SPECTRA OF PHTHALOXIME SALTS IN AQUEOUS PYRIDINE

The absorption spectra of the ammonium, sodium, potassium, and silver salts of the white oxime in pyridine solution containing 14 per cent water are plotted in fig. 5. The addition of water is necessary to dissolve the alkali salts, as their solubility in pyridine is slight.
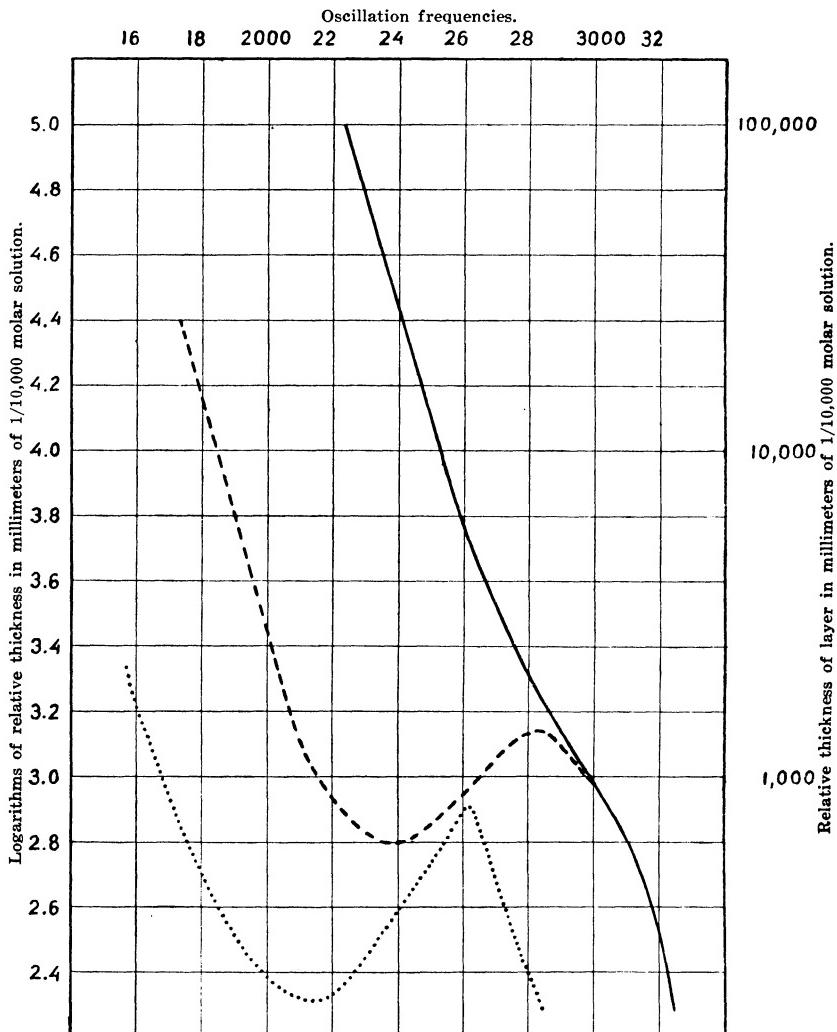
Fig. 4. Full curve = white phthaloxime in pyridine.
Dash curve = white phthaloxime in 50 per cent pyridine and 50 per cent water.
Dot curve = Silver salt of white phthaloxime in pyridine.
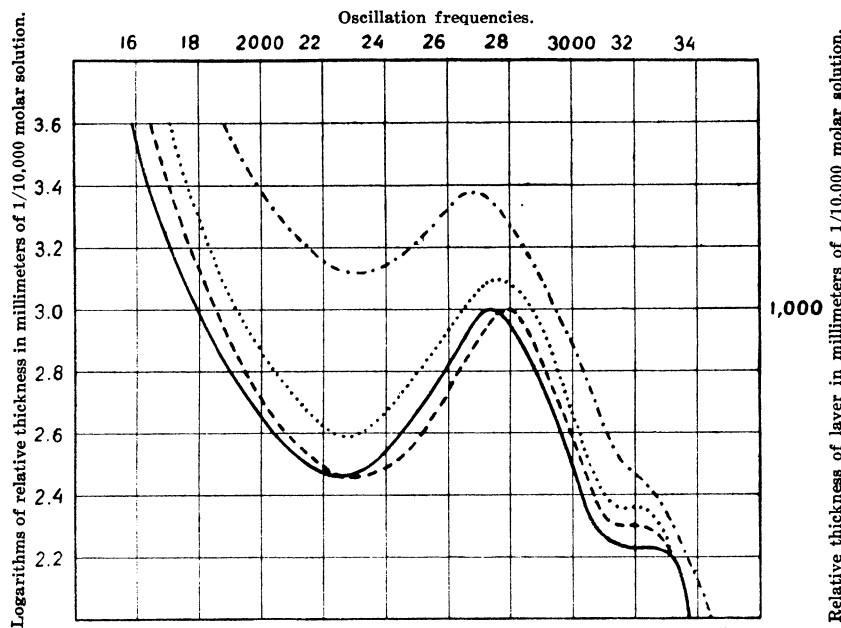
Fig. 5. Salts of white phthaloxime in pyridine containing 14 per cent water.
Full curve = silver salt.
Dash curve = potassium salt.
Dot curve = sodium salt.
Dash and dot curve = ammonium salt.

Description of fig. 5.—These curves bring out the difference in persistence and width of the color band and the corresponding residues of the ultra-violet oxime band. Since there is very little difference in the persistence of the latter in each case, it is reasonable to assume that the hydrolysis of the salts does not vary greatly in this solvent. The width of the color band and the dilution at which it appears are very different, especially with the weak ammonia base. These curves bring out the effect of different substituents and the relation between color and positive affinity better than any other series we have obtained. The addition product of silver salt and pyridine has been largely destroyed, and the absorption curve now heads at approximately the same point as that of the normal salts.

A solution of silver salt in alcoholic ammonia was prepared and photographed. The curve of its absorption spectrum falls between that of silver salt in pyridine and silver salt in pyridine containing 14 per cent water. This solution is unstable, and rapidly loses its red color with the formation of metallic silver. The addition product may be obtained by passing dry ammonia over

a weighed amount of silver salt in a porcelain boat. Decomposition occurs with gradual loss of weight in a few hours. The results of one experiment are as follows:

Substance (gram).	Gain (gram).	Gain (per cent).
0.2133	0.0153	6.81
	.0145	6.80
	.0123	5.76
	.0118	5.58

Calculated for

$C_8H_4O_3NAg \cdot NH_3$ 6.30

The boat and contents were then heated at 100° with a loss of weight corresponding approximately to the ammonia previously absorbed. The color remained a brownish gray, indicating no recovery of the original silver salt.

THE ACID SALTS OF PHTHALOXIME

When an alcoholic solution of phthaloxime is treated with alcoholic potassium acetate, an orange-colored crystalline salt is precipitated.[24]   A study of the absorption spectrum of this double salt clearly showed that in solution it was identical with the original oxime in the presence of one-half an equivalent of potassium ethoxide.   Sodium acetate forms a similar double salt which is more difficult to crystallize and isolate.   The underlying reasons for this fact are to be found in the relative solubilities of the normal sodium and potassium salts of phthaloxime. We have found that 100 cubic centimeters of absolute alcohol at 30° will dissolve 0.0590 gram of the potassium salt and only 0.0076 gram of the corresponding sodium salt.

Since the absorption spectra of the double salts were found to be identical with those of the oximes plus one-half an equivalent of corresponding alkali, we concluded that these salts could be crystallized from alcoholic solutions with equal ease by the addition of the proper amount of the hydroxide or ethoxide of the metal.   This was found to be the case, and the fact that sodium or potassium acetate dissociates in solution, giving a small excess of hydroxyl ions over hydrogen ions, explains why these double salts were originally obtained by the addition of alkali acetates, while the formation with alkali hydroxides was overlooked.   The double salts may also be prepared by mixing equal molecular equivalents of alcohol solutions of oxime and the normal alkali salt and concentrating to crystallization.

[24] Orndorff and Pratt, *loc. cit.*

COLORLESS ALKALI SALTS OF PHTHALOXIME

The effect of temperature upon molecular equilibrium is little understood, but there is undoubtedly a decreased activity at low temperatures. Alcohol solutions of phthaloxime show less yellow color when cooled in a mixture of solid carbon dioxide and ether. This may be due to a decreased activity of hydrogen toward the partial valencies of the unsaturated groups, or may be caused by a change in the equilibrium of molecular rearrangement. When a cold alcohol solution of sodium ethoxide was added to the above oxime solution, crystals of sodium salt were precipitated in an almost colorless form. These showed no increase of color as long as they were kept cold in the freezing mixture, but rapidly turned red after filtering from the mother liquor, due in all probability both to the rise in temperature and the condensation of water. The colorless crystals may be taken as the true oxime type of salt, regardless of which theory be applied to explain the colored compounds.

THE ABSORPTION SPECTRA OF PHTHALHYDROXAMIC ACID

Alkaline solutions of phthaloxime salts suffer rapid transformation into salts of phthalhydroxamic acid [25] with loss of identity between the white and the yellow isomer.[26] It appears that the difference between the two forms depends upon the integrity of the double bond between carbon and nitrogen, and that this is destroyed when the hydroxamic acid forms. Moreover, the free hydroxamic acid when heated in solution gives phthaloxime, the white isomer forming at 60° and the yellow at 100°. The formation of hydroxamic acid may be due to the increased activity of molecular vibration when hydrogen is replaced by a metal atom or to the tendency of the rearranged molecule to take up the elements of water. However, phthaloxime suspended in distilled water gradually forms hydroxamic acid upon standing even in the presence of mineral acid and without passing through a colored stage, so it is not essential to assume a different molecular condition as necessary for the transformation. Alkali appears merely to accelerate the rate of reaction, without influencing the final product. This is further evidence that the oxime and its salts possess identical molecular structure.

For purposes of photographing the absorption spectrum of the hydroxamic acid, alcohol solutions of oxime were treated with an excess of alkali and allowed to stand until colorless.

[25] Lassar-Cohn, *loc. cit.*
[26] Orndorff and Pratt, *loc. cit.*

Oscillation frequencies.
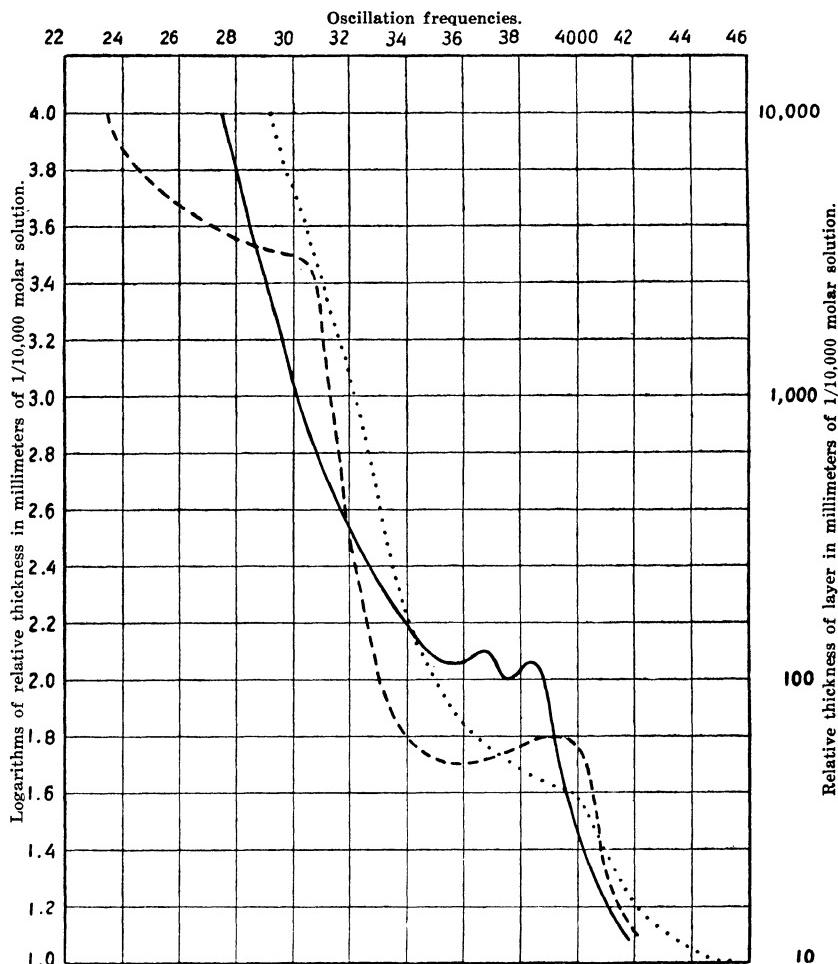
Fig. 6. Full curve = phthalhydroxamic acid.
Dash curve = phthalylphenylhydrazine.
Dot curve = anilidophthalamic acid.

Description of fig. 6.—The absorption spectrum of phthal-
hydroxamic acid shows a small band in the ultra-violet heading
at $\dfrac{1}{\lambda} = 3560$ and indications of benzene bands. This is evi-
dence that the condition present in oxime, phthalic acid, phthal-
imide, etc., is still present, although the persistence of the
characteristic band is greatly decreased in the case of the
hydroxamic acid. The spectroscopic behavior of phthalhydrox-
amic acid, therefore, corresponds with the formula generally
assigned to this compound.

ACTION OF PHENYLHYDRAZINE ON PHTHALOXIME

When an alcohol solution of either the white or yellow phthaloxime is gently warmed with phenylhydrazine, the following reaction takes place:

$$C_6H_4 \underset{\diagdown C=NOH}{\overset{\diagup C=O}{\diagup \diagup O}} \quad + H_2N \cdot NH \cdot C_6H_5 \quad \rightarrow \quad C_6H_4 \underset{\diagdown C \overset{O}{\diagdown NH \cdot NH \cdot C_6H_5}}{\overset{\diagup C \overset{O}{\diagdown OH}}{}}$$
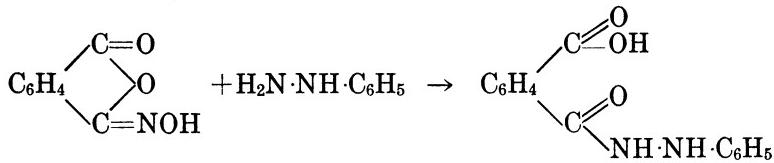
Phthaloxime.   Anilidophthalamic acid.

The anilidophthalamic acid thus formed was recrystallized from alcohol until colorless, and found to be identical with the compound described by Hötte [27] who obtained it from phthalic anhydride and phenylhydrazine.

0.1698 gram gave 17.2 cubic centimeters nitrogen over water at 31°.5; barometer, 763 millimeters.

	Calculated for $C_{14}H_{12}O_3N_2$ (per cent).	Found (per cent).
Nitrogen	10.93	10.96

0.1974 gram dissolved in absolute alcohol required 7.70 cubic centimeters of N/10 sodium hydroxide for neutralization. Theory, 7.71 cubic centimeters.

The absorption spectrum of anilidophthalamic acid is plotted in fig. 6, and indicates by the band heading at $\frac{1}{\lambda} = 3700$ that the structure is analogous to phthalhydroxamic acid and correctly represented by the above formula.

PHTHALYLPHENYLHYDRAZINE

If the alcohol solution of phthaloxime and phenylhydrazine be heated on the water bath for an hour, the reaction proceeds further with the splitting off of one molecule of water. A neutral yellow compound is formed identical with Hötte's phthalylphenylhydrazine. The same product results when anilidopthalamic acid is heated, the reaction going to completion rapidly at 100°. This compound crystallizes from alcohol in long yellow prisms, and melts at 182° uncorrected.

(1) 0.1854 gram gave 20.0 cubic centimeters nitrogen over water at 29°; barometer, 762.5 millimeters.
(2) 0.1740 gram gave 18.8 cubic centimeters nitrogen over water at 30°; barometer, 763.7 millimeters.
(3) 0.2230 gram gave 0.5761 gram CO_2 and 0.0821 gram H_2O.

[27] *Journ. f. prakt. Chem.* (1887), II, **35**, 268.

	Calculated for $C_{14} H_{10} O_2 N_2$ (per cent).	Found (per cent).
Carbon	70.58	70.44
Hydrogen	4.20	4.09
Nitrogen	. 11.76	11.82
		11.77

The absorption spectrum of phthalylphenylhydrazine is also plotted in fig. 6. It shows a well-developed ultra-violet band heading at $\frac{1}{\lambda} = 3600$ and a step-off extending from $\frac{1}{\lambda} = 2400$ to 3060. The characteristics of this spectrum throw grave doubt upon the symmetrical structure,

$$C_6H_4 \underset{C=O}{\overset{C=O}{<}} N \cdot NH \cdot C_6H_5$$
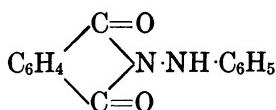
given by Hötte. We have found his method of preparation analogous in every way to the formation of phthaloxime from phthalic anhydride and hydroxylamine. The replacement of the oxime group of phthaloxime by the phenylhydrazine residue corresponds to similar reactions studied by Just,[28] and undoubtedly results in a similar structure. Moreover, a careful study of the absorption spectrum in comparison with those of various phenylhydrazines and osazones described by Baly and Tuck [29] and by Baly, Tuck, and Marsden [30] leads us to believe that this compound may not be a hydrazone. We hope to continue this investigation, and in a later article to present conclusive evidence concerning the structure of this interesting compound and its derivatives.

[28] *Ber. d. deutschen chem. Ges.* (1886), **19**, 1205.
[29] *Journ. Chem. Soc. London* (1906), **89**, 982.
[30] *Ibid.* (1907), **91**, 1572.

119480——4

ILLUSTRATIONS

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32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2

PLATE I. YELLOW PHTHALOXIME. 1/1000 MOLAR SOLUTION. THICKNESS OF LAYER, 32 TO 2 MILLIMETERS.

Fig. 1. Potassium salt of white phthaloxime in 90 per cent alcohol. 1/100 molar solution. Thickness of layer, 1, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 30, 50, 75, and 100 millimeters.
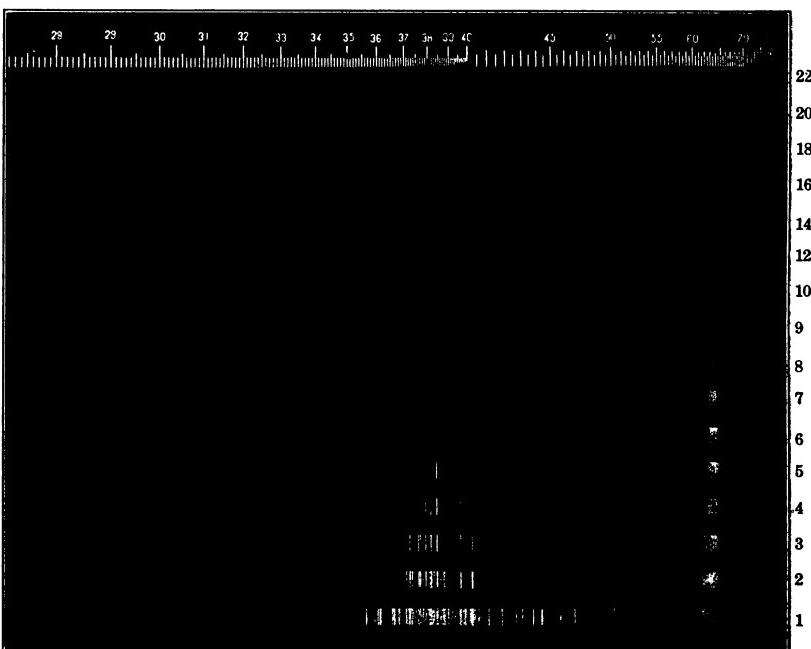
Fig. 2. Silver salt of white phthaloxime in pyridine. 1/100 molar solution. Thickness of layer, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, and 22 millimeters.

PLATE II.

THE OPTICAL EFFICIENCY OF TINTED GLASSES IN RELIEVING EYE STRAIN

By D. S. Pratt

(From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.)

One plate

In the Tropics, and during certain seasons of the year in temperate regions, the harmful effects of excessive bright sunlight on the eyes have been more or less mitigated by employing tinted glass. At the present time a large variety of colors and tints are supplied in blanks from which plane surfaces or lenses of any formula may be ground. The color or tint used has generally been a question of personal preference and skillful advertising, rather than the result of any data regarding the quality and quantity of light transmitted by the glass.

It is well known that ultra-violet light exerts an extremely harmful influence upon the retina of the eye due to its marked actinic property, and that prolonged exposure to light rich in these short wave lengths will cause blindness. Colorless glass is sufficient to cut off the greater part of the ultra-violet spectrum and give protection in special cases.

The various portions of the visible spectrum differ markedly in their physiological effect. The longer waves at the red end are more or less converted into heat radiations within the eye and act as an irritant, while those of shorter length comprising the indigo and violet possess greater actinic property and resemble the ultra-violet. The intermediate portion of the spectrum is, therefore, most restful, and ideal protection would be afforded by a glass capable of transmitting sufficient light throughout this portion while at the same time reducing the intensity of the red and eliminating the ultra-violet.

The different types of optical glass investigated were samples of various tints, carefully polished with approximately parallel plane surfaces.[1] Light from a nickel-iron arc was employed, and a Hilger spectrograph with special Cramer plates used in

[1] These samples were prepared and furnished by Messrs. Clark & Co., Manila, P. I.

photographing the various spectra. Table I shows the limits of the transmitted portion with the various glasses.

TABLE I.—*Spectra transmitted by various tinted glasses.*

Type of glass.	Range of transmitted spectra. Wave lengths.
Röntgen	3,035 to 6,990
Clear crown optical	2,970 to 6,950
Shade No. 1, blue	3,020 to 6,950
Shade No. 3, blue	3,030 to 6,950
Shade No. 5, blue	3,040 to 6,950
Shade No. 2, amber	2,980 to 6,840
Shade No. 3, amber	3,520 to 6,840
Shade No. 4, amber	3,845 to 6,840
Shade No. 6, amber	4,630 to 6,840
Shade No. 1, London smoke	3,220 to 6,940
Shade No. 3, London smoke	3,275 to 6,940
Shade No. 4, London smoke	3,320 to 6,940
Shade No. 5, London smoke	3,360 to 6,940
Shade No. 6, London smoke	3,460 to 6,940
Shade No. 1, amethyst	2,980 to 6,940
Shade No. 3, amethyst	3,005 to 6,940

Great accuracy cannot be attained by this means in measuring the limits of transmission at the red end of the spectrum. In the case of colorless glass the limit is dependent upon the sensitiveness of the plate toward the longer wave lengths. The tinted glasses show decreased intensity of the spectrum in this portion rather than well-marked selective absorption. The figures in the above table defining the red end of the transmitted spectra are included for relative comparisons rather than as definite limits.

The following table gives the wave lengths corresponding to the middle of the range covered by each of the seven primary colors, and is included for reference.

TABLE II.—*Wave lengths of the primary colors.*

Color.	Wave length.
Red	7,000
Orange	5,972
Yellow	5,808
Green	5,271
Blue	4,732
Indigo	4,383
Violet	4,059

The Röntgen and clear crown optical glasses transmit the entire visible spectrum unchanged, and only afford protection

from light of wave lengths below 3,000. The three shades of blue show practically the same limits, but in addition cause a reduction in the intensity of the red. This effect is so slight that these tints possess little to recommend their use. The four samples of amber differ greatly in the light transmitted. The light shade designated as No. 2 removes less ultra-violet than the blue, while the darker tint represented by No. 6 cuts off all the blue and indigo. This gives excellent protection from the short wave lengths, but fails to moderate the remainder of the visible spectrum to any great extent, and results in sharp contrasts that are not restful. Amber No. 4 is to be recommended when sharp definition is desired with the greatest protection possible under the conditions. In the great majority of instances this is not the case, and a glass combining the good features of the amber with a reduction of intensity throughout the visible spectrum is more to be desired.

The glass designated as shade No. 1, London smoke, shows a general reduction in all regions of the visible spectrum with the red eliminated to a slightly greater extent than the green and blue. The amount of ultra-violet cut off is not greatly in excess of that caused by clear glass, nor is the limit shifted to much extent by the darker tints, although the effect on the visible spectrum is progressively emphasized. The shade known as No. 6, London smoke, affords the most complete protection, but would hardly transmit sufficient light under ordinary circumstances. No. 4, London smoke, is probably the most satisfactory of all the glasses examined. It does not distort the color balance to which the eye is accustomed, as does the amber, but causes more the effect of natural shade and is consequently very restful. The larger proportion of short wave lengths transmitted by the smoke tints is of less importance than the general and correctly proportioned reduction in the visible spectrum.

The two shades of amethyst resemble the blue in their limits of transmission, and give selective absorption of so slight a character that they cannot be considered as supplying satisfactory protection.

It is hoped that this brief description of the optical behavior of various tinted glasses available for eye protection may render some assistance in choosing the most efficient color and shade for the purpose desired.

ILLUSTRATION

PLATE I. SPECTRA OF NICKEL-IRON ARC TRANSMITTED BY VARIOUS GLASSES.

THE RELATION OF SEISMIC DISTURBANCES IN THE PHILIPPINES TO THE GEOLOGIC STRUCTURE

By MIGUEL SADERRA MASÓ [1] and WARREN D. SMITH

(*From the Weather Bureau, and the Division of Mines, Bureau of Science, Manila, P. I.*)

Three maps

In the light of studies of the last ten years, stimulated by the tremendous cataclysms of Messina and San Francisco, entirely new principles have been introduced into the study of seismic disturbances of the crust of the earth. The old centrum theory of Mallet is generally discredited.

Beyond a doubt, many seismic disturbances are due to causes other than vulcanism. Many of the worst disasters we have experienced have nothing to do with volcanoes, and that volcanoes are nearby is only a coincidence, or may be explained by the fact that the place where great disturbances in the earth's crust occur is naturally a zone of weakness and where molten material would be expected to seek an outlet. At the time of the Messina earthquakes, Mount Etna, which can be seen from Messina, was comparatively quiet. The great disturbance at Messina, as is generally known, was due to an adjustment along the line of a

[1] Assistant Director of the Weather Bureau.

great fault in the earth's crust, which is marked by the Straits of Messina.

The work of the Italian Geologic Survey has demonstrated that these disturbances are propagated along very definite lines. So thoroughly did the Italian geologists do their work that by superimposing upon a geologic and topographic map of the Province of Calabria another map showing the location of cities and all the works of man, with all historical data regarding earthquakes, one can see at once that: (1) Certain points are more subject to earthquakes than others; (2) points removed from these lines have suffered less or not at all; (3) at intersections of these lines the greatest disasters occurred. These lines, which follow more or less definite systems, proved to be the projections of various earth lineaments such as fault lines, joint lines, formation contact lines, and axes of mountain ranges.

The great California earthquake of April, 1906, is a striking example of this. This earthquake was due to a dislocation along the well-known San Andreas rift, and, although the waves from this disturbance were propagated, to varying distances, on both sides, the greatest disturbance occurred along the line of this fault.

When one can indicate a point on a map and say definitely that here the crust of the earth is unstable, seismic geology is shown to be of very great practical interest to humanity in general and to engineers in particular, and especially is it pertinent in geologically young parts of the world like the Philippine Islands where mountain building is in progress and where the evidences of recent vertical movement of various portions of the island mass actually can be measured.

Concrete examples of what these disturbances mean are to be had in the earthquakes of Messina and of San Francisco and in the eruption of Taal Volcano.

The people of Messina had been warned repeatedly, but commercial interests were so great that they took no heed of their danger, and consequently millions of dollars worth of property as well as thousands of lives were lost at the time of that disaster. The same is true of San Francisco. The reported property loss at the time of that catastrophe amounted to 490,000,000 dollars.

The disturbances in the region of Taal were primarily due to the volcano, but Taal Volcano is located along a line of crustal weakness, and at that time a very appreciable displacement occurred along one or more lines passing through Taal Volcano.

One of these lines ran from the volcano to the coast through the town of Lemery, and the other from Taal Volcano to the barrio of Sinisian, making with the sea a triangular strip several square kilometers in area. This whole block dropped a meter or more, so that the sea washed inland for a distance of a kilometer over the main highway along this coast. The road between Lemery and Sinisian had to be reconstructed. The damage to buildings in the town of Lemery was considerable. Fortunately no very large structures were located along these lines, but had there been any the property loss would have been much more conspicuous. We may not see in our lifetime a recurrence of disasters either at Messina or San Francisco, but the time will surely come when there will be further displacement along these great earth rifts. It is true that there never will be as great disasters in the Philippines, due to the fact that most of the Filipinos live in basket-like houses which are the very safest at the time of an earthquake, but large engineering works have been constructed, others are being planned, and large public buildings are continually being built; hence it is of vital importance thoroughly to investigate this question in the light of all the data we now possess.

The scope of the present paper is: (1) To outline the physiography and geomorphology of the Philippines; (2) to discuss the kinds and distribution of the rock formations and the major structural features of the Islands; (3) in the light of these, to show the origin of each of the important seismic disturbances of the past; and (4) to draw some practical conclusions.

We are of the opinion that most of the seismic disturbances in the Philippines should be attributed not to volcanoes but to displacements along the major structure lines of the Philippine Islands. In view of the catastrophe of Taal Volcano and of eruptions at other points like Camiguin and Mayon, the layman is apt to have his perspective altered, and he is naturally prone to attribute certain phenomena to causes which are not causes but are results of factors not yet ascertained. It should be borne in mind that volcanoes are merely incidents in the growth of the Archipelago. Both volcanoes and earthquakes may be traced to the existence of lines of weakness and crustal displacements. Many earthquakes are due entirely to volcanic phenomena, but we believe we can prove that *the major earthquakes and the majority of earthquakes in the Philippine Archipelago are not due to vulcanism.*

Until the year 1863 nothing was written on Philippine earthquakes.[2] Even at the present time there exist but few papers based on modern seismologic principles, and all of these have been written during the last ten years.

The Manila Observatory from its foundation as a private institution in 1865 has directed its attention to earthquakes, but for many years its work was confined to segregating and publishing exact monthly observations without making a complete study of the subject. Its collection of monthly curves in which are contained the hourly observations of the Bertelli microseismograph is exceedingly valuable on account of the long period of time covered.

The earthquake of June, 1863, which practically destroyed the city of Manila and many of the neighboring towns and caused the death of more than 400 persons, led to the nomination of a commission to investigate the architectural character of the buildings and the nature of the soil of Manila in so far as these might be a source of danger in the future. As at that time the only engineers in the Philippines were those who were members of the corps of military engineers, the commission was formed from among these, but their work appeared to be limited to the establishment of several more or less successful principles and practical rules to which the plans of the new buildings to be erected in Manila were to conform.

Ten years later the commander of military engineers, D. Mariano Cortes y Aguillo, wrote a memoir on the same subject.[3] Notwithstanding the undoubted merit of this work as a practical guide for architects, little account was taken of it by the authorities, and it was not published until after the earthquakes of 1880. The author discusses the different seismic theories without adopting any of them regarding Philippine earthquakes. He concluded, after the examination of the damaged buildings and other existing data, that the most violent seismic movements in Manila are in an approximate north and south direction.

After the earthquakes of 1880, a commission composed of engineers of public works was appointed to study with care the ruins caused by these earthquakes, to point out the defects in the structure of the buildings that had been damaged, and to

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[2] The more or less accurate accounts of earthquakes which may be found scattered in the histories of the Philippines are not here considered.

[3] Los terremotos—Sus efectos en las edificaciones y medios prácticos para evitarlos en lo posible. Manila (1881).

formulate rules which would be more practical than the ones previously drawn up for the rebuilding and repairing of the city. This second commission, therefore, was not directly concerned with the study of the causes of the earthquakes of 1880, nor with the determining the extent and probable epicenter of the same. José Centeno, engineer of mines, was entrusted with this task. His memoir [4] is one of the best that has been published from a descriptive point of view. He personally covered the whole territory in which these earthquakes had been most violent, and hence was able to determine, with the precision possible in such cases, the meizoseismic areas of the three destructive earthquakes that took place from July 14 to 21, 1880.

It is to be regretted that in this investigation, which reflects much credit upon him, he did not direct his observations to the discovery of rifts and faults which would have indicated the nature of the dislocation, which took place in the Eastern Cordillera, and which were the causes of these earthquakes. He could not prescind from the ideas then prevalent of the relation of earthquakes to volcanoes, and, if he does not actually attribute the July earthquakes to the influence of Taal Volcano, at least he makes mention of several small eruptions which were supposed to have occurred in the same year, as though he wished to indicate in what direction investigations were to be made if there should be an inquiry as to the origin of those earthquakes.

A short time before this, Centeno had been sent on a commission to the Peninsula of Surigao where several very severe earthquakes had taken place in 1879 and which had left indelible impressions of their violence in the shape of numerous fissures and subsidences. In his report, he assigns Mainit Lake as the epicenter of the earthquakes. Like many other writers he supposed this lake to be an extinct volcano. He could easily have assigned another origin, because the great number of fissures and subsidences along the ridge of mountains and especially in Point Bilat—which is its extreme northwest extension—made it rather clear that their character was tectonic. It may be that some spasmodic movement had occurred which had closer relation to the slower geologic movements in this part of the island, and it was these the author took cognizance of, since he quotes as proof that the depth of the port of Surigao had changed during the earthquakes of 1879.

[4] Temblores de tierra ocurridos en Julio de 1880 en la Isla de Luzon. Madrid (1885).

Six months had scarcely elapsed since the Manila earthquakes when a large series of seismic movements began in Nueva Vizcaya which lasted from January until November, 1881. Enrique Abella y Casariego, engineer of mines, was commissioned to visit the affected province, to investigate as to what likelihood there was of any greater seismic cataclysm happening in the future, and if there were to see if it would be possible to make the inhabitants emigrate to other provinces not so affected. Abella's work [5] is a very able and complete study of the local and superficial character of the earthquakes and of their probable duration, and his predictions with regard to their continuance were perfectly realized, for as he prognosticated the earthquakes ceased shortly afterward, and up to the present no other of any great importance has occurred. In his discussion of the origin of these earthquakes, this author shows that he, too, was influenced by the current volcanic theories and hence searched for possible connections between the Province of Nueva Vizcaya and Mayon Volcano which a short time before had shown signs of greater activity.

The Pangasinan earthquake of 1892 gave Abella the opportunity of writing another interesting memoir.[6] In this work he does not limit his studies to the earthquakes, but adds many valuable notes on the geology of Pangasinan, La Union, and Benguet Provinces, thus coming more into line with modern seismologists. Notwithstanding this, when he draws his final conclusions, he places most weight on the existence of volcanic rocks and other volcanic signs and remains, both ancient and modern, as if it were impossible to discover the origin of these earthquakes without recurring to volcanic action either directly or indirectly.

Several other very interesting and useful geologic monographs are due to the indefatigable labors of Abella.[7]

In 1895 Saderra Masó [8] published a book on earthquakes in which he did not pretend to give a complete seismologic study,

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[5] Terremotos de Nueva Vizcaya en 1881. Madrid (1884).

[6] Abella y Casariego, E. Terremotos experimentados en la Isla de Luzon . . . en Pangasinan, Union y Benguet. Manila (1893).

[7] Apuntes fisicos y geológicos de Nueva Vizcaya. Madrid (1884). Rapida descripción física, geológica y minera en bosquejo de la Isla de Panay. Manila (1890). El Mayón ó Volcán de Albay. Madrid (1885). Emanaciones volcánicas subordinadas al Malinao. Madrid (1885). El Monte Maquiling y sus actuales emanaciones volcánicas. Madrid (1885). La Isla Biliran y sus azufrales. Madrid (1885).

[8] La Seismologia en Filipinas. Manila Observatory (1895).

but merely a coördinated collection of data which might serve as a basis for the future study of the earthquakes of the Philippine Archipelago. Many of these data were in the archives of the Manila Observatory and had not been published previously, while others were to be found scattered in histories, periodicals, and other publications.

The only important conclusion he draws is that the *seismic center dangerous for Manila does not lie in the existing volcanoes south and southeast of the city, but in the eastern range of mountains and especially in the part east-northeast and northeast of Manila.*

The same writer[9] has given accounts of the more important earthquakes that have taken place in the different parts of the Archipelago. During the first period he endeavored as a rule to trace a relation between earthquakes and volcanoes. In the second period—that is, 1900 to 1912—he inclined to the more modern ideas in certain of his papers,[10] although he exaggerates the importance of volcanic manifestations when he speaks of the different epicenters of regions of greater seismic activity.

Since 1907 this investigator has written several short papers[11] on the seismicity of the different regions of the Archipelago as a preparation to a more complete work like the present. In these articles he has attempted to indicate by the alignment of the different epicenters the possible existence of seismotectonic lines, in conformity with the recent principles of seismology.

In 1899, Koto[12] published a valuable study in which he discusses the different tectonic lines and volcanic belts of the Philippines and their connection with Celebes, Borneo, and the Moluccas. It is a thorough and complete study of great value,

[9] Monthly Bulletins of the Manila Observatory, 1890 to 1897, and from 1900 to 1912.

[10] Report on the seismic and volcanic centers of the Philippine Archipelago. Manila (1904); Volcanoes and seismic centers of the Philippine Archipelago. Washington (1904), as part of the census of the Philippine Islands.

[11] The earthquakes of Ambos Camarines, *Bull. P. I. Weather Bur.* (1907), 172; The earthquakes of the Batanes Islands and southern Formosa, *ibid.* (1909), 97; The seismic centers of northern Luzon, *ibid.* (1909), 131; Submarine seismic centers near the coasts of northern Luzon, *ibid.* (1909), 167; Seismic centers near western Mindanao and Jolo, *ibid.* (1909), 203; Seismotectonic lines in southern Luzon, *ibid.* (1911), 409.

[12] On the geological structure of the Malayan Archipelago, *Journ. Coll. Sci., Imp. Univ. Tokyo* (1893), 5, pt. II, 2.

and must be taken into account when drawing the tectonic lines of the Philippines.

As a general study of the geology and vulcanism of the Philippines, Becker's report [13] is the most complete work that has appeared. In it is to be found an excellent résumé and criticism of all the writings on the subject that had been published up to that date. A shorter but more recent work is the article by Smith.[14]

The names of several Austrian, German, and French geologists and explorers to whom we owe the first geological data on the Philippines should also be mentioned. The principal ones are: von Richthofen, Carl Semper, Oebbecke, K. Martin, Jagor, Roth, R. von Drasche, and J. Montano. Likewise, attention is called to the works of the eminent French seismologist, Montessus de Ballore, who published many articles on Philippine earthquakes during the years 1895 to 1901. In one of his books [15] he gives a summary of these articles on the earthquakes of the Philippines. This author must be considered as the first to apply to this Archipelago the principles of modern seismology by referring its earthquakes, not so much to imaginary volcanic agencies, as previous authors had done, but to the principal and geological accidents; in other words, to tectonic lines. Hence, the chapter referred to above must in justice be reckoned the first and most important contribution to the study of Philippine seismology.

SUMMARY OF THE PHYSIOGRAPHY OF THE PHILIPPINE ISLANDS

To present a clear idea of the underlying causes of seismic disturbances in the Philippine Islands, it is necessary to make some general statements. The Philippine Islands form a link in the chain of outliers of the old Australasian continent. According to the "horst" theory of the formation of continents and ocean basins, the Philippine Islands lie at the very edge of the Asiatic horst. In June, 1912, the German survey ship *Planet* sounded to a depth of 9,780 meters about 60 kilometers off the northeast coast of Mindanao.[16] Soundings to the west-

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[13] Report on the geology of the Philippine Islands, *21st Annual Rep. U. S. Geol. Surv.* Washington (1901).

[14] The essential features of the geology of the Philippine Islands, *This Journal, Sec. A* (1910), 5, 307.

[15] Les tremblements de terre. Paris (1906).

[16] *Zeitschr. Ges. Erdk.* Berlin (1912), No. 6, 471; No. 8, 629–631; carte des sondages du "Planet" à l'Est des Philippines, à 1: 15,000,000, Abt. 31.

ward of the Philippines have not yet located anything like such tremendous depths. We may then conceive of the Philippine Islands as being at the edge of the continental platform or on the brink of a tremendous "Graben" (Plate I). This platform was subsequently raised above sea level and complexly folded at the time of what is known as the "Miocene revolution" which extended from New Hebrides through the Philippines northward to Japan; westward across Burma, India, Persia, and Egypt; northward to the Vienna basin; and westward even to the Pyrenees. Following this crumpling of the crust, a gradual tilting of the Philippine block toward the east seems to be going on at the present time. This is evident from the raised coral reefs on the western coast of northern Luzon, the western coast of Palawan, and from the raised deltas and beaches on the western coast of Zamboanga Peninsula with the existence of drowned river basins which we know of as certain on the eastern coast of Luzon, and at other points in the Archipelago about which we can conjecture although we have no definite information.

Von Richthofen,[17] ten years ago, noticed a peculiarity of the Philippine Archipelago in connection with the Japanese, Riu Kiu, Kurile, and Aleutian chains of islands; namely, a series of arcs with their convex sides turned toward the Pacific. One of these arcs is well marked in the Philippines by the tectonic line passing through southeastern Luzon, Samar, and the Eastern Cordillera of Mindanao. Northern Luzon does not conform very well to this arc, but we may imagine that there has been a fault and offset at the narrow portion of Luzon at the northern end of Tayabas Peninsula.

Besides this dominant curved line, and those parallel to it in the eastern part of the Archipelago, there are in the Philippines several other distinct tectonic lines as shown in Plate II. One of these is the Palawan line, another is the Sulu Archipelago line, others are the parallel lines through Panay, Negros, and Cebu—all trending northeast and southwest. Masbate seems to be the "keystone" in the Philippine structure. The eastern prong of this island conforms closely with the outermost arc of the Archipelago, while the western prong conforms with one of the northeast-southwest lines passing through eastern Panay.

[17] Geomorphologische Studien aus Ostasien, *Sitzungsber. d. k. pr. Akad. d. Wiss. z. Berlin* (1902), **40**, 944–975.

Taking up the physiography of the Islands in detail, there is in the northern part, on Luzon, to the eastward, first a cluster of volcanoes containing Bulusan, Mayon, Isarog, and Iriga; then the narrow Albay Plain; west of this a belt of Tertiary sediments; and farther west a trough occupied by Ragay Gulf. The anticlinal, marked by Tayabas Peninsula, consisting of folded Tertiary sediments, lies west of this; then the volcanic group consisting of Banahao, Cristobal, and Arayat; west of these, the central plain of Luzon, partly a tuff plain and partly made up of alluvium; and farthest to the west a line of extinct volcanoes marked by the Zambales Cordillera. In northern Luzon a zonal arrangement exists, but is not so marked. Recent volcanoes are few, Caua in Isabela Province being the only one we know of in that section.

In the Visayan Islands there is this same general zonal arrangement of formations, but the evidence of vulcanism is not so marked as in Luzon. The islands are marked by anticlines and the narrow straits by synclines.

This is likewise true of Mindanao. Along the eastern coast there are recent and Tertiary sediments flanking a core of igneous rocks on the immediate west, and dipping eastward toward the "fossa," or trough, just east of Mindanao; then the great Agusan trough; west of this an interrupted volcanic chain marked by such prominent points as Matutan and Apo; the great alluvial flat occupied by the Rio Grande de Mindanao; the regular zone of volcanic peaks marked by Malindang and the old craters south of Lake Lanao and those in the unexplored region south of the Rio Grande; farther west a belt of folded Tertiary sediments; then the synclinal marked by Sibuguey Bay; and last, the anticlinal marked by Zamboanga Peninsula.

Cross folding, probably with faulting, has broken up the Philippine block in such a way as to produce numberless islands in line with the main tectonic lines running through the larger islands.

Types of mountains.—Of the various kinds of mountains such as folded, block, and volcanic mountains, the two dominant types in the Philippines are the first and the third. We suspect the existence of mountains of the block type in some places where we have not sufficient data to prove it. It might seem at first sight that the majority of the mountains of the Philippines are volcanic, but these are merely superimposed upon the folded mountains or are located along other lines of weakness. While

there are a few active volcanoes in the Philippines, most of the volcanoes are extinct, or dormant, as shown by the many worn-down volcanic stocks, preserving in varying degrees their former outlines.[18]

The principal folded mountains are the Central Cordillera of Luzon, the Eastern Cordillera which has its southern contin-uation in Tayabas Province, and the cordilleras of Cebu, Leyte (?), eastern Mindanao, and various other parts of the Islands.

Block mountains are rare in the Philippine Islands, but at Bambang on the main line of the Manila and Dagupan railway in Luzon there are some hills which are due to the Tertiary sediments being tilted up like blocks. From the railroad the tilted beds are seen presenting a bold escarpment to the east, undoubtedly due to a fault, but dipping gently to the southwest.

On Panay Island the secondary ranges—those flanking the Central Cordillera—are tilted blocks of Tertiary sediments. The strike of these secondary ranges conforms exactly to the strike of the sediments. Their eastern slopes correspond in-variably to the dip of the formations. On the upstream side the slopes are precipitous where the upturned edges of the sandstone and the shale beds can be seen. Displacements along the bedding planes of these formations are frequent and have undoubtedly given rise to many local quakes.

Kinds of rocks.—Before discussing the tectonic features of the Islands it will be necessary to consider the distribution of the various classes of rocks. We have the following kinds to con-sider: (*a*) Deep-seated igneous, (*b*) extrusives, (*c*) intrusives, (*d*) Tertiary and older sediments, (*e*) metamorphic rocks, (*f*) recent alluvial and pyroclastic deposits.

(*a*) The deep-seated igneous rocks are diorite, gabbros, pyrox-enite, peridotite, and syenite. These rocks have all been fully described by Iddings.[19] Their distribution is the principal thing of importance in this discussion. The deep-seated rocks are

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[18] These various volcanoes have been taken up in other articles in more or less detail. The centers of volcanic activity at the present time are Taal Volcano in Batangas Province; Mount Mayon in Albay Province, Luzon; Mount Canlaon in Negros; and Camiguin Island just north of Misamis, Mindanao. All of these volcanoes have been in eruption within the last ten years, and to them can be attributed many of the minor seismic disturbances to which the Archipelago has been subjected.

[19] *This Journal*, Sec. A (1910), **5**, 155.

naturally not very widely distributed on the surface and usually are found only in the cañons of the central ranges. They are particularly abundant in northern Luzon, throughout the Central Cordillera; in Palawan Island; the Western Cordillera of Panay; the Central Cordillera of Cebu and Leyte; the Eastern Cordillera of Mindanao; on Masbate Island; in fact, wherever the streams have been able to cut through the overlying, more recent formations.

(*b*) In all parts of the Islands there is a large amount of extrusive material which forms a mantle over the deeper lying formations. Naturally these are found around the volcanic areas, and these extrusives are very pronounced in the Zambales Range of southwestern Luzon and in various parts of the Central Cordillera lying above the old igneous and the Tertiary sediments. In the Central Cordillera of Luzon there exist great patches of andesite, marking probably early Tertiary volcanoes. In the Zambales Mountains there is a development of andesite, marking probably a still later period of volcanic activity. On Mount Arayat, which rises isolated out of the central plain of Luzon, basalt occurs, and around Taal Volcano and on the Binangonan Peninsula there is a considerable amount of basalt. Extrusives are particularly well developed in the southeastern volcanic cluster of southeastern Luzon, comprising the well-known peaks of Bulusan, Mayon, Isarog, etc. They are found overlying much of Masbate, particularly in the central portion; also in western Panay, a portion of Cebu, most of northern Negros, central Leyte, and notably in Mindanao, there being a broad belt of extrusives running north and south through the Apo and Matutan Ranges. Also, there is a great patch of basaltic material around Lake Lanao and a great volcanic mass, of which Mount Malindang is the center. There is also great development of these extrusives covering almost the entire Islands of Basilan and Jolo and the lesser islands of the Sulu Archipelago.

As yet, we know of extrusives in Palawan only in the northern part. The principal mountainous mass of Mindoro, Mount Halcon, is largely andesitic.

There is one general conclusion which can be drawn from the distribution of the extrusives in the Philippine Islands; namely, that the entire recent volcanic activity consists, as far as we know, of basaltic materials, and the older stocks are without an exception andesitic.

(c) Small and large intrusions of diorite, granite, and basalt are innumerable throughout the Islands. In the Central Cordillera of Luzon the intrusions seem to be generally diorite. They cut both the Tertiary sediments and the overlying extrusives. In the Province of Ambos Camarines in southeastern Luzon granitic intrusions cutting the diorite and possibly the sediments can be seen. In the Sulu Archipelago we have found a number of small basaltic intrusions cutting some of the recent sediments. Owing to the absence of an accurate base map of the Philippine Islands and the fact that our work has been largely of a reconnaissance nature, these intrusions have not been mapped in detail or with sufficient accuracy for us to state whether or not they follow any general system of jointing or earth lineaments.

(d) Flanking all the cordilleras on both slopes there is a greater or less development of sandstones, shales, and limestones which have been bowed upward in the general Miocene uplift referred to above, with some minor crumpling at various points. The folding in the northern part of Luzon has apparently been a gradual and gentle uplift of the strata. In Tayabas Peninsula the flexures are sharper. In the Zamboanga Peninsula the strata have been so intensely compressed that schists are the result. These schists have been considered by some to be older than the Tertiary, but there seems to be no good reason for not referring them, in part at least, to the Tertiary. The central portion of Mindanao consists of gently folded sediments. The major axis of folding in the Philippines is in general north and south; along the outside arc of the Islands, northwest and southeast; on the inside, northeast and southwest; but in central Mindanao in the Cotabato Valley the axis of folding is more nearly east and west.

(e) Metamorphic rocks occur more or less pronounced in various parts of the Islands. In the Province of Ilocos Norte there is a considerable development of schist, and in Ambos Camarines there is schist and gneiss along the border of the granite intrusion referred to above. Schists have been found at one locality in the Central Cordillera of Cebu; at various points in Palawan; on the Zamboanga Peninsula alluded to above; in the Province of Bukidnon, Mindanao; on the Surigao Peninsula and just east of the Gulf of Davao; at one point on the Tayabas Peninsula; and on the Caramoan Peninsula, southeastern Luzon. These schists appear to be for the most part metamorphosed sediments.

(*f*) Recent alluvium from the mountains deposited upon coral shelves results in a greater or less development of coastal plains around all of the islands. The coastal plains are for the most part negligible, but some of the intermontane plains are very important. The northern three-quarters of the central plain of Luzon is largely alluvium. The Albay Plain is largely alluvium as is the case in the great valleys of the Cagayan, Agusan, and Cotabato Rivers. Also, the central plain of Panay shows a very considerable accumulation of detrital material.

Around Manila we have, in addition, a great area of pyroclastic material which is cut through by the Pasig River. This is known from well logs and river sections to be at least 100 meters thick.

TYPES OF SEISMIC DISTURBANCES

Modern seismology, in rejecting every agent and force exterior to our planet as causes of earthquakes, reduces the classes of shocks to the following three types: volcanic, tectonic, and rockfall.

Many examples of these three types are to be found in the seismological records of the Philippine Weather Bureau, and a few of the more characteristic will be briefly mentioned.

To the *volcanic type* belong all those earthquakes that are intimately connected with volcanic eruptions caused by explosions or sudden outbursts of steam. These volcanic earthquakes, contrary to popular belief and to the ideas generally held for many centuries by scientists, are in reality of but slight importance and occur only in certain restricted districts.

The recent eruption of Taal Volcano, January 27 to February 8, 1911, offered a very typical series of these earthquakes. On the night of January 27, severe earthquakes occurred on Luzon and in adjacent regions, while at the same time or very shortly afterward it was noticed that the principal crater of the volcano increased in volcanic activity. This activity as well as the frequency and intensity of the shocks went on increasing during the 28th and 29th, until at approximately 2.26 on the morning of the 30th there took place the greatest and most destructive eruption recorded in the history of the volcano. After this paroxysm of eruptive activity the volcano returned to its normal state in a short time, although the earthquakes continued to be very frequent during the three following days, January 31 and February 1 and 2, thus indicating that there was still an accumulation of energy in the interior of the volcano. During

the eruptive period—January 27 to February 7—995 shocks were recorded in the Manila Observatory, all of them between I and V of the Rossi-Forel scale. Some of the principal shocks were perceptible at a radius of from 120 to 200 kilometers. The meizoseismic area of the earthquakes was a prolonged zone which took in not only the volcano itself, but also the south-southwestern part of Laguna de Bay and the bordering territory as far as the sea, some 20 kilometers away (Plate II).

The decrease of perceptible intensity of the seismic action outside the epicentral area was, according to many comparisons made on the spot, 1 degree of the Rossi-Forel scale for every 15 kilometers. The same result was also deduced from the fact that the maximum intensities of several of the earthquakes as felt in Manila, a distance of 63 kilometers, were from IV to V of the scale, while in the epicenter, judging from the effects in the ground and on buildings, they were from VIII to IX. These same earthquakes, which had an intensity VIII to IX in the epicenter and IV to V at a distance of 63 kilometers, were also registered at Taihoku (Formosa) some 1,000 kilometers away, but not in any more distant observatory.

The reports of previous eruptions of Taal also make mention of numerous volcanic earthquakes, which no doubt possessed the same characteristics as those that occurred recently. A curious fact is noted in these reports; namely, that while in the recent eruption the meizoseismic area extended 20 kilometers to the south-southwest, in the previous eruptions it extended to the north-northeast for about 30 kilometers as far as Laguna de Bay. From this it is easy to recognize the direction of the rift on which the volcano originated.

In 1871 a series of volcanic earthquakes occurred on the volcanic Island of Camiguin, north of Mindanao. These earthquakes culminated in the opening of a small crater whose activity lasted four or five years. They were first felt in February, and went on increasing in intensity and frequency until the morning of April 30, when the volcano exploded and the earthquakes suddenly ceased. The greater number of these shocks were perceptible on the island only, although many were also heavily felt on the neighboring coasts of northern Mindanao and southern Bohol, while only four or five, whose intensity in the epicenter was between VII and X, were noticed at a distance of 250 kilometers.

The following table gives some idea of the number and intensity of the shocks preceding the eruption of Camiguin.

TABLE I.—*Number and intensity of shocks preceding the eruption of Camiguin.*

[Reported from Camiguin.]

Date.	Earthquakes.	Remarks.
Feb. 16 _____	Two slight earthquakes _____	
17 _____	Frequent shocks during day and night_____	
18 _____	_____do _____	One of intensity VIII.
19 _____	_____do _____	One of intensity VII.
20 _____	_____do _____	
21 _____	_____do _____	One of intensity IX.
22 _____	_____do _____	One of intensity VIII.
23 to 28 _____	_____do _____	
Mar. 1 to 3_____	_____do _____	
4 _____	_____do _____	One of intensity VI.
5 to 7_____	Less frequent; not more than 10 per day ___	
8 _____	_____do _____	Two of intensity VI.
9 _____	_____do _____	
10 _____	_____do _____	Do.
11 to 13_____	_____do _____	
14 to 17_____	Less frequent; 4 or 5 per day _____	
18 to 19_____	More frequent and violent than during preceding days.	
20 to 31_____	Less frequent; not exceeding 6 per day ____	
Apr. 1 to 29_____	Frequent during the entire month; number never less than 6 to 10 per day.	
30 _____	At 7 a. m., with a terrific detonation and emitting a cloud of vapor, rocks, and ashes, a volcano burst on the north-northeastern end of the island, only a few meters from the shore. After this explosion, semifluid lava continued to rise quietly for about three years, building up a cone approximately 400 meters high. The ashes of the first explosion were carried to distances of 200 kilometers. Within a radius of 2 to 3 kilometers from the new crater, the destruction was complete. The earthquakes ceased almost completely a few days after the eruption. There was no loss of life as the people of Catarman, the town nearest to the volcano and the only one destroyed by it, had deserted their homes long before, some having left for other islands as early as the end of February.	

The *tectonic type* of earthquakes is caused by the sudden relief of strains, due to contractions and foldings in the crust of the earth; when these pass the limit of equilibrium and the modulus of elasticity of the crust, they give rise to rents and fractures and other sudden movements of more or less severity depending on the degree of the accumulated strain. This type

comprehends the greater number of earthquakes felt in all parts of the world and in particular all those of greater intensity and extent. To it belong practically all the great Philippine earthquakes enumerated by Saderra Masó [20] and especially those which occur in eastern Mindanao, in the Valley of the Agusan, and on the Pacific coast, regions which appear to be closely related to the great submarine trough, "the Philippine deep" of 9,780 meters, already referred to. Further on we shall discuss some of the tectonic earthquakes of greater importance.

The *rockfall type* embraces the earthquakes of small extent, which, having their focus or seat of origin at a slight depth, are brought about by the fall of rock in caves and underground passages, by landslides, and in certain cases by the settling of superficial rock masses displaced by tectonic seismic motions. It appears that this is the predominant type of shocks felt in several nonvolcanic regions of the Philippines, but earthquakes of this type are very often extremely difficult to recognize on account of the distance between the seismic stations and the large extent of the uninhabited mountainous and forest districts in which they occur, so that it is impossible to fix the limits of the area where many of the earthquakes are perceptible. We consider as typical instances of this class of earthquakes those of 1881 in Nueva Vizcaya. From January to October of that year there was a continuous series of earthquakes, the maximum of intensity and frequency occurring in September. To get an idea of this seismic period, the well-known catalogue of the missionary Xavert should be consulted. This catalogue takes in sixty-three days between January and October, and contains the record of 196 earthquakes with the times at which they occurred. Phrases such as "almost continuous," "many more," "the whole day," "the whole night" appear twenty-five times in the list, thus indicating that the smaller earthquakes were not counted.

Abella, who examined the effects of these earthquakes in the field, found that the meizoseismic area was of very small extent and that its center coincided with the town of Bambang. The great majority of the shocks were only perceptible within an area of 60 kilometers, so that only 5 of intensity VII to IX exerted any influence beyond the province. Much of the data supplied by Abella fully confirms his statement which is further strengthened by an examination of the records of the hourly

[20] Catalogue of violent and destructive earthquakes in the Philippines, 1599–1909. Manila (1910).

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observations of the Bertelli microseismoscope or tromometer made in the Manila Observatory.

With the catalogue of Xavert before us, these observations have been examined again, and we have not been able to find any movement which could coincide with the Nueva Vizcaya earthquakes other than the ones corresponding to the larger shocks mentioned above and three or four other doubtful ones. The experience of seventeen years shows us that this tromometer, still in use at the Observatory, indicates perfectly all earthquakes of any great extent and of intensity III or greater whose epicenter lies within a radius of 200 kilometers from Manila.

Abella deduced from these facts that the seat of origin of the earthquakes must be very superficial and of small extent, and hence the conclusion that there was little likelihood of any greater ones happening in the future was fully verified.   Such earthquakes could not in any way be classed as tectonic, and hence the author attributed them to volcanic influences, suggesting that the subterranean forces, which at that time had given greater activity to Mayon Volcano, might possibly have extended toward the northwest and affected the Province of Nueva Vizcaya, some 400 kilometers from Mayon.   After an examination of Abella's report, it seems evident that the earthquakes of Nueva Vizcaya belong to the rockfall type; and this opinion is strengthened by a consideration of the topography of the province.   The whole province is an elevated mountainous region of the nature of a plateau separated from the plains of Luzon to the south by a line of steep cliffs, while on the west it is bounded by a series of peaks whose precipitous western slopes rise abruptly from the deep cañon of the Agno River.

Besides the earthquakes of Nueva Vizcaya, many of those that take place in the Mountain Province, which comprises the former districts of Benguet, Bontoc, and Lepanto, possibly are of the same character.   In many parts of this region, particularly in the western side where coraliferous limestone predominates, recent fractures and subsidences are to be met with at every step.   The same might be said of other parts of the Archipelago having a similar geological structure.

DISTRIBUTION OF SEISMIC DISTURBANCES

In the Philippines as in all other seismic regions of the globe, most earthquakes originate along determined lines which constitute special features of the topography of the Archipelago.

If we add to the Catalogue of violent and destructive earthquakes in the Philippines 1599–1909, cited above, the earthquakes

which have occurred since that time, we have the distribution of tectonic epicenters [21] as given on the map (Plate II).

The region which has suffered the most from violent earthquakes during the past fifty years is without doubt eastern Mindanao and particularly the Agusan Valley. We have no seismic data of this region from a period more remote than 1889, but this is doubtless owing to the undeveloped state of that part of the Archipelago and to the consequent lack of communication with the outside world. The great deep-sea trough which exists along the east coast of this part of the island indicates that many earthquakes must have occurred there since it first began to form. The same may be said of the coasts of Samar which also are exposed to the influence of the same "deep," and hence that they also are as unstable as the eastern coast of Mindanao. The principal epicenter of Samar is near the northeast coast.

In the Island of Mindanao there exist also the following seismic regions: The Gulf of Davao and the district of Cotabato between Apo Volcano and Illana Bay; the coast along Illana Bay and the district of Lanao; the extreme western part of the island near Zamboanga. Basilan Island and the Sulu Archipelago are also in a region of great seismicity, although the epicenters seem to lie in the neighboring seas. The district of Dapitan in the northwest is affected by a submarine epicenter situated between Dapitan and southern Negros. All the central part of northern Mindanao comprised within the district of Misamis appears to be a region of much greater stability, but the neighboring Island of Camiguin has suffered much at different times from volcanic earthquakes.

The Visayan Islands, in addition to what has already been mentioned of Samar, have two regions of great seismicity, Panay and Leyte. An epicenter lies in the Iloilo Straits between Panay and Negros, while within the Island of Panay at a distance of about 30 kilometers from the southeast coast there is another more important one where originate very violent earthquakes, but apparently of the rockfall type. In Leyte there are two volcanic epicenters, one in the southeast and the other in the north and northeast, and there is probably a rockfall epicenter to the west close to the Camotes Islands.

The Islands of Cebu and Bohol, and perhaps also Oriental Negros, may be considered as stable. However, Oriental Negros

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[21] The word "epicenter" is used in the broad sense, as the region where important earthquakes originate.

was very probably in the past the scene of many volcanic earthquakes, although the data we possess are very deficient. Volcanic formations more recent than the Pliocene do not occur in Cebu.

The principal seismic regions of southeastern Luzon and adjacent region are those of Camarines, Albay, and Masbate with three principal and well-defined epicenters—the first along the central depression of Ambos Camarines, the second to the north of San Bernardino Strait, and the third in the Island of Masbate or near its northern and southern coasts. Between Sorsogon Bay and the Gulf of Albay there is also an epicenter of small extent.

The southern part of Luzon constitutes the second seismic region of greater importance in the Archipelago. Four epicenters may be distinguished in it; namely, one in the east near the coast which appears to stretch from the north of the Bay of Lamon to the south in the sea between Mindoro and Marinduque; a second between Mindoro and Luzon; a third in the China Sea along the coasts of Cavite and Zambales; and the fourth, which may be called the Manila epicenter, is situated in the Eastern Cordillera and its spurs, between Laguna de Bay and the Gulf of Baler. The volcanic epicenters of Taal and other volcanoes are not reckoned.

Northern Luzon from parallel 16° northward contains 4 extensive seismic regions: That of Pangasinan whose long axis appears to cross the island approximately from east to west from Casiguran Bay to Lingayen Gulf, following the edge of the great central plain of the island. The Nueva Vizcaya epicenter may be considered as belonging to this central seismic region. The second region includes the various epicenters of Ilocos Sur and Norte, some of them in the sea close to the coast, others probably at the extreme east of the plain or coastal belt which borders these provinces. The third region, which is an important one, is situated along the central mountain chain of the Mountain Province, and extends as far as the Babuyanes Islands. Within the confines of the extensive Cagayan Valley there are very important tectonic lines, but they have not, since 1645, given rise to any very great earthquake. However, there are frequent earthquakes of slight extent and intensity, those occurring in the north being probably of volcanic origin, while those in the south are due to epicenters whose influence seems to decrease.

In the extreme northern part of the Archipelago and outside the limits of Luzon there are at least two epicenters close to the

meridian 122° east—one stretching from the volcanic Island of Camiguin to the northeast coast of Luzon and the other not far from the Batanes Islands.

In Luzon, therefore, no province is free from the effects of earthquakes, for although it is true that in some, such as Tarlac, La Union, Isabela, Cavite, and Pampanga, no epicenter seems to exist, still they are affected by the movements which originate in other provinces.

Seismotectonic lines.—The map, Plate II, gives the location of the principal seismic areas (red ellipses) of the Islands (the stars indicating the principal epicenters in these areas) and the general direction of certain principal mountain chains. Each figure includes one or more epicenters, and shows the general shape and extent of the meizoseismic areas corresponding to the greatest earthquakes which have occurred within the region limited by the same. The figures 3, 5, 7, 8, 9, 10, and 20 bear a heavy line to indicate that the earthquakes originating near the same place have been too many to be specified. Twenty-five different areas are recorded, and 5 of these (12, 13, 15, 17, and 18) are undoubtedly due in large part to rockfall and volcanic activity, the other 20, in our opinion, being due to tectonic causes. This is probably quite contrary to the general belief regarding the earthquakes in the Philippines. The tectonic areas are 1 to 11, 14, 16, and 19 to 26. *The areas of greatest seismicity are 2, 3, 4, and 21, where at the present time there is no known volcanic activity and where probably there has been none since the end of the Tertiary period.*

Following the methods of other students of seismology, we have connected the various epicenters shown on the map by lines and have also added a few more of the latter where no epicenters are indicated. There is a remarkable coincidence between these lines and the principal lineaments in the Philippines. The various lines are denoted *A—A, B—B,* etc., on Plate II so that they can be easily referred to.

Line *A—A,* which is drawn through many epicenters, passes through the northwest corner of the Province of Ilocos Norte, follows approximately the coast west of the city of Vigan, and then cuts across the northwest portion of Pangasinan Peninsula. It is impossible definitely to state whether this line marks a fault line which lies along the coast, or is due to a contact between the recent sediments and the older rocks which here lie close to the coast, but we are of the opinion from geological studies in the Province of Ilocos Norte that the latter is true.

There is a very small development of coastal plain in this region and also rocks of doubtful age which may possibly belong to the Jurassic against which these very recent sediments abut. There is also a considerable

development of raised beaches and raised coral reefs along this coast, making it plain that elevation has taken place along this line in recent times. Whether this elevation has been accompanied by differential movement, we are unable to say.

There are no evidences of recent volcanic activity in any part of the region, but granites, schists, and some very old andesite are present.

Line *B—B* connects epicenters of northern and southern Luzon, cuts through Dalupiri, the westernmost of the Babuyanes Islands, then very closely follows the Central Cordillera southward through the Agno Valley, thence to the eastward of the Zambales Range, and on through the Island of Mindoro, where it cuts the latter west of the great volcanic stock of which Mount Halcon is the principal peak. There is no information with regard to the rocks on Dalupiri. However, the rocks of the Central Cordillera in Luzon have a core of plutonic rock, chiefly diorite, flanked by Tertiary sediments which have been arched upward, and in various points along the crest of this arch extrusive rocks can be found in abundance. No volcanic activity now manifests itself in that region, but it is a region of hot and of salt springs. It is a line along which there was considerable extrusion of igneous rocks in the past, but there is no evidence of this now; therefore, seismic disturbances which take place along this line at the present time are due to displacement along a line of weakness rather than to any volcanic activity. *It is significant that all of these points where either past or present volcanic activity is manifested are found to lie along more or less definite, and in many cases, straight lines.*

Line *C—C* is the next prominent line which runs at right angles to the *B* line, and lies either on, or very close to, 4 epicenters. At the upper end of the central plain of Luzon the mountains rise rather abruptly, and present a front which has a general east and west direction. It is possible that this line represents a fault line where the central plain represents the downthrow side. That area has not been studied in detail, but it appears as if there is a definite break along that line. In a more arid region one would expect to find definite escarpments facing southward, but in a region of high rainfall like the Philippine Islands these escarpments naturally would very soon be obliterated so that their existence can only be inferred.[22]

D—D is a very prominent line which runs along the Archipelago close to the 122d meridian. It connects the epicenters of the Batanes Islands, Cagayan Valley, Casiguran Bay, east of southern Luzon and Mindoro, and west of Mindanao. The northernmost part of the line, outside of Luzon. follows very closely the Batanes and Babuyanes volcanic chain, studied by Ferguson[23] and represented by the cones Yami, Mabudis, Inem, Iraya, Balintang Rocks, Babuyan Claro, Camiguin, and Didicas. Within Luzon it passes not far west of Caua Volcano, southward along the structural Cagayan Valley, following the trend of the Eastern Cordillera until this turns toward the southwest, or rather when it seems to be interrupted by the gap forming Casiguran and Baler Bays. From the latter bay it follows the eastern coast of Luzon and passes to the Mindoro Sea through the volcanic region of Tayabas Province. Farther on toward the south it passes fairly close to Tablas Island which is oriented in this

[22] Herrmann, Raf., *This Journal, Sec. A* (1911), **6**, 331.

[23] Manuscript report.

direction, thence to the west coast of Panay, ending finally between Basilan and Jolo. The general topographic features suggest that this is a very characteristic tectonic or structural line, although definite geological reconnaissances are wanting to confirm such a hypothesis.

Line *E—E* passes through many epicenters. It lies just west of the epicenter near Bayombong, Nueva Vizcaya, passes through some epicenters near the east coast of Luzon and Lamon Bay and at the southeast corner of Leyte, and connects with the epicenters located around the northern point of Surigao Peninsula. This line is seen to conform to the Central Cordillera of Leyte, to the coast range of Masbate, and the syncline marked by Ragay Gulf; but we are not certain that it conforms to any particular lineament in Luzon, as it passes through country about which there is little geological information. There are closely folded sediments whose strike is northwest-southeast in the eastern portion of Masbate, and Adams[24] has visited Leyte and mapped the cordillera showing its axis to be approximately along this line.

Line *H—H*, which has been called "The Taal Volcano line,"[25] starts from the northwestern part of Mindoro and in a nearly northeast direction crosses Taal Volcano, the western portion of Laguna de Bay, extending into the Eastern Cordillera, east of Manila, and thence runs toward Baler and Casiguran Bays. The southern portion of this important line from Mindoro Strait to Laguna de Bay has been accurately identified;[26] while the probability of its continuation across the Eastern Cordillera toward the Pacific has been demonstrated by Saderra Masó. This line passes through the epicenter of Manila, located in the Eastern Cordillera, east and east-northeast of this city.

Line *F—F* is located along the epicenters west of the Zambales coast and another located a short distance north of Mindoro. It intersects several of the lines, already mentioned, near Cape Santiago, southern Luzon. It does not follow any well-marked rift, but follows approximately the trend of the Bataan coast of Luzon.

Line *G—G* begins north of Mindoro, passes along the western coast of Cavite, follows the western border of the Central Plain, across Pangasinan Province, and thence along the axis of the coastal ranges of La Union Province. A displacement along this line would account for the earthquakes described in charts VI, X, XIII, XV, XVI, XIX, and XXIII[27] with their epicenters apparently around or in the northern part of Manila Bay. It is a contact line between andesite with the alluvium of the central plains and between Tertiary sedimentaries and igneous rocks in Union Province.

Line *I—I* cuts through the Dapitan epicenter and three others which lie close to it. It also follows approximately the long axis of the Island of Cebu and of the Zamboanga Peninsula, but it is drawn west of the axis of the Zamboanga Peninsula as it is believed that some earthquakes have originated from displacements along the west coast of this peninsula.

Line *J—J* does not pass through any very important epicenter, but cuts through San Bernardino Channel and follows the east coast of

[24] *This Journal, Sec. A* (1909), 4, 339.

[25] Saderra Masó, Miguel, *Bull. P. I. Weather Bur.* (1911), 409.

[26] Pratt, Wallace E., The eruption of Taal Volcano, *This Journal, Sec. A* (1911), 6, 63.

[27] La Seismologia en Filipinas. Manila Observatory (1895).

Panay, passing through the center of the Island of Guimaras. We have drawn a line along these points for the reason that there is a contact on the Island of Guimaras between recent sediments to the westward and the igneous rocks found toward the east. It is our belief that the earthquakes which have been experienced on the eastern coast of the Island of Panay are due to displacements along this contact. The continuation of this line also might explain the trend of this coast of Panay.

Line *L—L* passes through an epicenter at the southern point of the Island of Samar and another near the end of the southeastern prong of Leyte, through the Island of Camiguin on which is located a dormant volcano, and then follows the trend of Misamis Bay, in Mindanao, and finally passes close to an epicenter situated in the middle of the sea between Cotabato and Zamboanga. Formations at the lower end of Samar and Leyte are but little known, but there is the volcano on the Island of Camiguin mentioned above, and where the line crosses Mindanao there is more or less basalt. Misamis Bay probably marks some sort of a rift in the formations.

Line *M—M* passes through many epicenters in the Island of Mindanao. It intersects the *L* line at a point east of Dumanquilas Bay, passes through an epicenter west of Pollok, then follows very closely the trend of the Cotabato River to the point where the river turns northward, and thence through an epicenter east of Mount Apo. From here it passes close to an epicenter located in the sea east of the southeastern point of Mindanao. Note the agreement between this line and the lower course of the Cotabato River which is probably more than a coincidence.

Line *N—N* connects important epicenters in Camarines, Nueva Vizcaya, Samar, Leyte, and the northeast coast of Mindanao. It passes through the narrow Strait of San Juanico, separating Samar from Leyte, and along the Camarines Valley northwestward it strikes the eastern coast of Luzon, south of Casiguran Bay. In the Albay Valley it follows the contact line of the northern volcanic cluster along which the most violent earthquakes of the Camarines seem to originate, probably due to differential movements between the sedimentaries and the volcanic area, or possibly in the sedimentaries alone. Farther in the interior of Luzon this line would pass very close to the Nueva Vizcaya epicenter, but this epicenter is considered as rockfall.

Line *N'—N'* is a secondary one which would pass through the Sorsogon and northern Samar epicenters. This line nearly coincides with the contact between the sedimentaries and extrusives, west of Sorsogon; eastward it follows the alluvial and littoral deposits of the lowland extending from Sorsogon to Gubat. In San Bernardino Strait and in the northern part of Samar it nearly conforms to an indentation of the "Philippine trough," along which are located some epicenters affecting Catanduanes, Albay, and northern Samar.

Line *O—O* begins close to the epicenter at the southern point of Samar, continues southward to the Island of Dinagat, through the epicenter at the northern point of Surigao Peninsula, then approximately conforms to the Matutan Range, through the epicenter near Mount Apo, and finally passes through the Island of Sarangani. We do not know the composition of the rocks of the central part of the Island of Dinagat, but on Surigao Peninsula crystalline schists flanked by Tertiary and recent sediments have

been noted. In the neighborhood of Lake Mainit the rocks are volcanic, although a short distance east of this body of water is a belt of metamorphics. In the Matutan Range the rocks are largely extrusives of more or less recent date.

Line *P—P* passes through three epicenters and along very important structural lines in the Archipelago. Beginning at the north, it passes between the Islands of Catanduanes and Luzon, through Batan Island, south through an epicenter near Biliran Island, and thence through an epicenter located near the southern end of Leyte. From here it extends through one in Butuan Bay, thence traversing very closely the structural line of the Agusan Valley in Mindanao, and finally emerges from Mindanao near the town of Mati. Very little is known about the geology of the parts of the Archipelago traversed by this line. In the Island of Batan the rocks are largely sedimentary; however, their strikes do not coincide with this line at all.

The Agusan Valley in Mindanao is very clearly a structural valley. What the condition of the rocks is, with depth, we do not know, as the alluvial filling in the Agusan trough conceals everything. This line is one of the most important in the Archipelago, and has been described in previous articles.[28] In the first of these Saderra Masó says:

"We call this line the 'Line of the Agusan River Valley' because *the portion of it which lies within the said valley has been the seat of the greatest number of violent earthquakes which occurred during the last fifty years.*[29] The first seismic district of importance of this line comprises the large Gulf of Davao, which is 120 kilometers long and 50 to 70 kilometers wide. The average depth of this basin is 800 meters, increasing, however, toward southeast in such manner as to exceed 1,650 meters west of Cape San Agustin. * * * To the west of the gulf rise the gigantic Apo Volcano, the Matutun and several other cones of less importance, which constitute the northern boundary of the volcanic zone extending, as it seems, from Mount Apo as far as the Celebes, * * *.

"The extensive valley of the Agusan River runs from south-southeast to north-northwest, almost parallel to the east coast of Mindanao, * * *. The entire bottom of the Agusan Valley consists of marine sediments containing an abundance of recent shells: only at the mouths of the water courses, which descend from the mountains bounding it east and west, is found gravel containing well-worn pebbles of andesite and other igneous rocks. Every geologist who has visited this part of eastern Mindanao received the same impression, to wit, that its emersion from the sea is of quite recent date, and its elevation is still increasing. Some of them assigned the post-Pliocene period as the epoch of the formation of the sediments found in the Agusan Valley, * * *. This valley and the Davao Gulf appear to be portions of one and the same synclinal."

Line *Q—Q* begins near Placer on the northeast coast of Surigao Peninsula, and passes through an epicenter in Butuan Bay and the

[25] Saderra Masó, Miguel, *Bull. P. I. Weather Bur.* (1910), 283; (1911), 225.

[29] Italics are ours.—Authors.

northern course of the Rio Grande Valley. This line seems to be necessary to explain the anomalous course of this river. Line *O* and line *M* seem to explain this satisfactorily.

Numerous other lines might be suggested, but we have included all for which we have any geological basis and a few others as suggestions.

DISCUSSION OF IMPORTANT EARTHQUAKES

In discussing the various important earthquakes, little will be said about those previous to 1870, save the greatest which occurred in 1645, but we shall consider the entire series represented by the charts published in La Seismologia en Filipinas, and discuss most of them separately.

Earthquake of 1645, Luzon (3–9).[30] This earthquake compares favorably in magnitude with the greatest mentioned in the history of the world; its meizoseismic or epicentral area was not less than 490 kilometers from north to south; that is, from the southern coast of Batangas and Tayabas to the northern part of Cagayan. On the western coast it seems to have been of less intensity, at least the chronicles of the time are silent about its effects in these parts, while they deal very much with the destruction caused in Manila and neighboring provinces of the south, east, and north, and the tremendous effects produced as far north as Lalloc. in the Cagayan Valley, and in the eastern part of the Central Cordillera; that is, in the Mountain Province. That such an earthquake was due to tectonic movements, there cannot be the slightest doubt; furthermore, it is very certain that its origin was along a north and south line and that this line was within the Island of Luzon and not beyond its eastern periphery; it may be reasonably supposed that it was along the seismotectonic line *D—D*. The question arises whether the dislocations which then occurred along that line or fault were of such proportions as to be responsible for the many singular topographic features now existing along it in the Provinces of Nueva Ecija, Nueva Vizcaya, and Isabela. Moreover, as the origin of that earthquake seems to have been very close to the city of Manila, our opinion is that some dislocations occurred at the same time along the fracture represented by the line *H—H*. Similar occurrences of lines crossing each other are frequent in severe earthquakes. For example, the earthquake which occurred in 1870, having its epicenter in the northwestern portion of Luzon, apparently was

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[30] Figures refer to Plate II and indicate the location.

of tectonic origin, and might be explained as due to a displacement along the line A—A.

The great number of earthquakes which occurred in 1871 were of volcanic origin, having as their epicenter the Island of Camiguin. The destructive area includes Camiguin, Bohol, and that part of Mindanao known as Misamis; also, the southwest corner of Leyte.

Earthquakes of July 11 (3) and of November 5, 1871 (17), are both clearly of tectonic origin. The destructive area in the case of the first comprises the Central Cordillera of Luzon; and that of the second is located along line E—E or, perhaps, line P—P.

Earthquake of December 29, 1872 (7). The destructive area comprises roughly that portion of Luzon adjacent to line F—F, but it is possible that these disturbances originated from the Taal Volcano fracture. No eruption of Taal Volcano is recorded for this year.

Earthquakes of August 25 (22, 23) and October 16, 1874 (8, 9). In the former, the destructive area comprises the Zamboanga Peninsula, and is clearly tectonic, probably due to dislocations along the line I—I; in the latter, the destructive area comprises the region east of Manila Bay, more or less elongated north and south, and possibly has some connection with the line D—D. Taal Volcano was probably not the cause of this disturbance.

Earthquakes of May 1 (7, 8) and of July 5, 1877 (10, 11). The former was felt over most of southwestern Luzon, probably emanated from Taal Volcano, and probably was due to movements propagated along the line G—G which follows the western limit of the central plain of Luzon. The latter may have been of volcanic origin, as the whole southeastern volcanic region is comprised in the destructive area, or it may have had its origin in some movement along the line marking the Philippine "deep" (X—X).

Earthquakes of August 13, 1878 (7, 8), and of July 1, 1879 (17). The former seems to have had its epicentral area located near Manila Bay, resulting from disturbances along the line G—G mentioned in the last paragraph. The latter had its destructive area in northeastern Mindanao and Surigao Peninsula, and was possibly due to the Agusan line, but more likely to displacements along the line E—E.

Earthquakes of July 14 and 25, 1880 (5, 6, 8, 9). The destructive area shown on this chart indicates that the disturbances originated somewhere in the Eastern Cordillera of Luzon.

Two originated along line *H—H;* and the third, in the eastern part of Laguna Province, along line *D—D.*

The earthquakes of July 25, 1880 (5, 8, 9), show that the destructive area conforms pretty closely to that shown in chart VII. These should both be classed as tectonic.

Earthquakes of May 15 (4, 5, 6, 8) and of July 11, 1881 (15). In the case of the former, the destructive area is confined to the Eastern Cordillera in north-central Luzon, and is clearly of tectonic origin. That of the latter had its center on the Island of Guimaras, just south of Panay. This is clearly of tectonic origin, and it was probably due to displacements along the contact between the Tertiary sediments of the western half of the island and the igneous rocks of the eastern half.

The earthquake of July 16 in Ilocos Norte Province, Luzon (2), was undoubtedly due to disturbances along the line *A—A.*

Earthquakes of September 10, 1881 (5). The area of destruction during these earthquakes was very local, being in the southern part of Nueva Vizcaya, and may be attributed to purely local causes, possibly rockfall.

The earthquake of September 30, 1881 (4, 5), again centers in Nueva Vizcaya, and was probably of the same origin as the previous one.

Earthquake of April 30, 1882 (7, 8). The destructive area was very local and was centered just north of Manila Bay, but more to the westward near the contact between the material of the valley floor and the volcanic rocks of the Zambales Mountains, hence there seems to be some reason for conjecturing that it is due to tectonic causes. On September 12, a very similar earthquake occurred in the same region.

Earthquakes of July 25 (7, 8) and 28 (2), 1882. During the former, the epicentral area is situated between Taal Volcano and the China Sea, and hence may be of volcanic origin. That of July 28 is located along the Cordillera of Luzon in the northern part, and hence may be called tectonic.

The earthquake of September 11, 1882 (7), has its focus somewhere near Taal Volcano.

Two earthquakes on September 17 (10) and 21 (2, 3), 1882. In the case of the former, the destructive area is centered about the southeastern volcanic cluster in Luzon. The latter has its epicenter in north-central Luzon, but the longitudinal axis of the destructive area runs slightly north of east. We do not know of any prominent structural line in that region running in that direction. The course of the Abra River, where it makes a sharp right-angled bend to the west in the latitude of Vigan,

is suggestive of some prominent earth lineament. On September 6, 1862, October 9, 1901, and May 25, 1907, very similar earthquakes occurred in the same region, having their main line of propagation in nearly the same direction.

On October 10, 1882, there was an earthquake, the destructive area of which centers about San Miguel Bay in southeastern Luzon (10). Very little is known about the formation on the Caramuan Peninsula, so that we are unable to give any theory for the disturbances here.

Two earthquakes of February 10 (3, 4) and of July 14, 1883 (10). The former originated in the Province of Nueva Vizcaya, and probably was due to causes already mentioned. In the latter, the earthquake clearly originated from volcanic disturbances, as the destructive area comprises the southeastern volcanic region of Luzon.

Earthquake of July 27, 1883 (7, 8), is clearly volcanic, or at least related to the fracture passing through Taal which is included in the destructive area.

Earthquakes of January 10 (10) and March 22, 1884 (5). Both of these were very likely of tectonic origin; one had its epicenter in the northwestern portion of Pangasinan Province where there is no sign of recent vulcanism. This probably is due to displacements along line G—G. The second one had its epicenter near the southeastern volcanic region, but on the west side of the peninsula, where there is a slight uplift of Tertiary sediments, which may indicate this to be due to tectonic causes. Lately, in 1907, there occurred two destructive earthquakes in the same region, probably due to the same causes.

Earthquake of April 20, 1884 (7). This was not destructive, but, according to the distribution of the effects of the earthquake, it probably was of tectonic origin and can be attributed to displacements along line G—G.

Earthquake of October 29, 1884, had two destructive areas (6, 8, 9) more or less separated, the epicenter of one being just north of Laguna de Bay and the other just north of the southeastern volcanic cluster (10). As there is no sign of a volcano at present north of Laguna de Bay, it is probable that the line H—H runs through this region.

Earthquakes of December 17 and 24, 1884 (5, 13), are clearly of tectonic origin. In the former, the displacement undoubtedly took place along the line C—C; and that of the latter was probably due to movement along the line which runs northwest and southeast, through the straits between Leyte and Samar, which is indicated by the line N—N.

Only one earthquake (2, 3) is shown on this chart, and that seems clearly to have originated along line A—A.

Earthquakes of July 23 and 24, 1885 (5, 6). The first seems to have its epicenters northwest of Dapitan Peninsula. In 1897 another destructive earthquake occurred under the sea in the same region due to the same origin. It is very likely that this is of intertectonic origin, due to line I—I. There is no record of any volcanic demonstration emanating from the Dapitan Peninsula. It seems very clear from the great lineal extent of the destructive area of this earthquake north and south that the line I—I is responsible; hence this would be called tectonic. The earthquake of the 24th of the same month seems to be similar to that of December 17, 1884.

Earthquake of November 16, 1885 (7, 8). This is clearly of volcanic origin as it seems to have been most generally felt in the southwest volcanic region of Luzon.

Earthquake of November 19, 1885 (5), is similar to that of July 24, 1885, and is also tectonic.

Earthquakes of April 10 (15) and August 2, 1886 (7). The first one is undoubtedly tectonic and is connected with line J—J. The second may be in part volcanic, but, on account of its extension to the northwest, we believe that it can be referred to the tectonic line G—G.

Earthquakes of February 1 (3) and 2, 1887 (14). The former seems to have been localized in north-central Luzon and may or may not be tectonic. It is possible that this disturbance was due to rockfall. The latter earthquake seems to have affected the whole Island of Panay, and was probably due to rockfall, because a recent examination of this island has shown that landslides of considerable magnitude are of frequent occurrence on this island. In these two regions violent earthquakes of like character and probably of the same origin occurred in 1902 and 1904.

Earthquake of March 24, 1887 (10), was unquestionably of volcanic origin due to disturbances in the southeastern volcanic cluster of Luzon. The two earthquakes here shown of June 19 (6, 8) and October 1, 1887 (10, 11, 12), respectively, were only light ones. The second one emanated from the same volcanic region as the earthquake just mentioned, but that of June 19 was undoubtedly of tectonic origin in the Eastern Cordillera.

Earthquakes of June 27 (20, 21), May 3 (2, 3), and August 19 (4), 1888. The first is undoubtedly tectonic as we know of no volcanoes anywhere in that portion of Mindanao, but we

also do not know enough about the geology of that portion to say with any certainty that there is a tectonic line running at an angle to the main Agusan line. The reader is referred to an article by Saderra Masó [31] on this subject. On Plate VIII of that paper the author has indicated the several epicentric areas near the "Philippine deep." Most of these areas are elliptical, with their long axes extending north and south or northwest and southeast, but one of these has its long axis extending slightly north of east and south of west. The second seems to have had its center in the Cordillera of northern Luzon. The third is a clear case of movement along line *D—D,* or the Cagayan line.

Earthquakes of January 1 (17), February 5 (22, 23, 25), May 26 (7, 8), and of October 6, 1889 (17, 20, 21). The first is clearly due to movements along line *E—E;* and the second, to movements along line *M—M.* The third without question is due to the lines or fractures *H—H* and *F—F.* The fourth affected the whole Agusan Valley region, and the eastern coast can be attributed to the "Agusan line," or rather to the Pacific structural "deep."

In addition to the above list of earthquakes in the article La Seismologia en Filipinas, we desire to add the following important earthquakes.

Earthquake of 1892, Pangasinan, Benguet, and La Union Provinces (5). The nature of this earthquake seems to be tectonic beyond doubt, since it occurred in a region where no recent volcanic formations are to be found. The northern part of its epicentral area comprises the uplands of Baguio, where the tremendous upheavals which occurred in recent geologic periods are clearly evident. Almost in the center of the epicentral area rises Santo Tomás, an andesitic block mountain due in part to faulting, while in the southern part lies the alluvium of the Pangasinan plains. It seems highly probable that the cause of this earthquake can be found in some important dislocation which occurred near the Santo Tomás mountain mass. This epicenter belongs to line *C—C.*

Earthquake of 1893, Agusan Valley, Mindanao (20), is unquestionably the greatest which has occurred in this region during the last three centuries. The permanent sinking of part of the floor of the valley and the faulting on the divide between the headwaters of the Agusan Valley and the Gulf of Davao suggest a folding movement of the Eastern Cordillera as a

[31] *Bull. P. I. Weather Bur.* (1910), 279.

whole or a slip toward the east in connection with the changes which possibly occurred in the deep trough running along the east coast. Therefore, this earthquake must be classified as most typically tectonic, as it occurred along a most definite structural line.

Earthquakes of 1897. The fearful happenings of this year bring to the mind the somewhat fabulous occurrences of 1641, when earthquakes in Luzon occurred at the same time as eruptions in Mindanao, Jolo, and Sanguir. During this year destructive tectonic earthquakes were felt in northern Luzon (2), northern Samar (11), Masbate (12), and eastern and western Mindanao (19, 22, 23, 24), while as a climax Mayon Volcano had one of its worst eruptions. The most typical and important of these earthquakes was the one occurring in western Mindanao. Its origin or epicentral area seems to have been under the sea, west of Zamboanga Peninsula, where two very important lines, *I—I* and *D—D*, intersect. It must be considered as one of the most memorable of Philippine earthquakes on account of the most extraordinary seismic wave ever noticed in the Archipelago. Furthermore, it seems to have been connected with the rising of some temporary islands near the northwest and northeast coast of Borneo.

Earthquake of 1902, Illana Bay, Mindanao (23), shook heavily the districts of Cotabato and Lanao; its epicentral area comprised part of the bay, where the telegraphic cables were broken and buried under mud; the eastern coast and plain of Cotabato; and the northern coast with the uplands of Lanao district as far as the lake. In this last region there had been great volcanic activity during the Tertiary period, as is shown by the basalt flows which cover it and by some old volcanic cones rising toward the south and east; but, during the historic period, only one doubtful eruption is reported. Consequently, considering the wide extension of this earthquake and its effects upon land and the bottom of the sea, it should be classified as tectonic and connected with line *M—M*.

Earthquake of November 8, 1912, Sorsogon. The meizoseismic area of this earthquake where it was felt with intensity VIII–IX, causing considerable damage, was rather small, being only some 35 kilometers long by 10 kilometers broad. It took place in the town of Sorsogon, the mountains to the north and northwest, part of the coast toward the west, and the lowlands extending toward the south-southwest as far as Gubat. Its center nearly coincides with the contact between the volcanic

and the alluvial formations. Plate III shows the isoseismals of this earthquake and the geology of the region.[32]

The Sorsogon epicenter lies on the secondary seismotectonic line *N'—N'* which future events may prove to be, as it has been stated elsewhere,[33] the continuation or a branch of the Camarines line *N—N*.

It has been suggested by Mr. Wallace E. Pratt that this earthquake was due to differential movement between the igneous and the sedimentary block to the eastward and northward as shown on the map. This seems to be highly probable.

PRACTICAL CONSIDERATIONS

1. The fact of the instability of the earth's crust has been proved time and again both by tremendous catastrophes and by laboratory experiments. It has been demonstrated that many of these devastating earth movements take place along definite lines of weakness in the crust. The location and extent of these lines can usually be fairly accurately determined by a geological examination.

2. The points of intersection of such lines are dangerous as can be shown by an examination of the Province of Calabria in Italy.[34]

3. Volcanoes are only incidental phenomena, and are results rather than causes. They are usually found to be lined up along some rift line.

4. Points of danger in the Archipelago are:

> *a.* Along the Taal rift line from the town of Lemery to Los Baños on Laguna de Bay, and possibly farther to the northeast.
> *b.* All "made" land and recent alluvium. The California Earthquake Commission (1908) reported that the intensity of the shocks and the destruction were greatest and the amplitude of the waves longest in the "made" ground.[35]
> *c.* The Agusan Valley, Mindanao.
> *d.* The Straits of San Juanico.
> *e.* The district northeast of Manila near the east coast and northwest of the Island of Polillo. Three prominent lines intersect in two places close together in this region.
> *f.* That part of Batangas Peninsula which ends in Cape Santiago.

[32] Adams, G. I., and Pratt, W. E., *This Journal, Sec. A* (1911), **6**, 449.

[33] *Bull. P. I. Weather Bur.* (1912), 447.

[34] Hobbs, W. H., Some principles of seismic geology, *Beiträgen zur Geophysik* (1907), **8**, 224.

[35] Report of California Earthquake Commission. Washington (1910).

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5. Types of structures best suited to Philippine conditions:

    a. Bamboo houses. All the parts of a bamboo house are tied together with rattan. These houses are strong, elastic, and light, and behave like immense baskets.

    b. "Strong material," locally used to distinguished wooden, well-nailed houses from bamboo structures. Floor joists well anchored.

    c. Sand-lime brick tied to steel frame should be cheaper than concrete, and in case of warping walls can be removed easily and new steel put in.

    d. Reënforced concrete, perfectly safe if properly made, but expensive and apt to receive permanent warping and fissuring [*] from the twisting motion of some earthquakes.

Ordinary brick walls with roof of unanchored tiles make one of the worst possible types of construction as demonstrated at Messina.

6. The necessity of geological examinations of all dam, pipe line, and bridge sites should be emphasized. Tremendous damage was done to these kinds of engineering structures in the San Francisco earthquake. It is well known that the breaking of the water mains by the earthquakes left the city at the mercy of the fires which shortly broke out.

7. The Harbors of Cebu, Iloilo, and Zamboanga, owing to their approximating the shape of a funnel or double funnel, are more or less in danger from tidal waves.

8. Manila Harbor, owing to the comparatively small entrance and rapidly widening basin, should be entirely safe in this respect.

SUMMARY AND CONCLUSIONS

There is a close relationship between seismic disturbances and geologic structure.

The majority of earthquakes are of tectonic origin, in the Philippines, at least.

Volcanoes are secondary phenomena.

The area of greatest seismicity in the Archipelago is in the Agusan Valley, Mindanao.

There is a close relationship between the orographic and other geomorphic lines and the lines connecting the principal epicenters in the Archipelago.

Seismic disturbances can be studied and disasters can, to a large extent, be avoided.

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[*] In the severe Sorsogon earthquake, November, 1912, a new school-house of reënforced concrete and concrete blocks was considerably damaged in both portions; the reënforced concrete portico sustained more or less fissuring.

ILLUSTRATIONS

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SKETCH MAP OF THE
"Philippine Deep."

Soundings in meters.

Adapted from the map published by
Wilhelm Krebs in Geogr. Zeitschr.
Vol. 19 3rd Hft. Mch 1913.

P A C I F I C　　O C E A N

SAMAR

LEYTE

BOHOL

CAMIGUIN I.

BUTUAN
BAY

M I N D A N A O

DAVAO
GULF

Bernardino Strait

Surigao Strait

DINAGAT I.

SIARGAO I.

5000
4000
3000
6000
7000
8000
•8900
6000
9788
9000
9020
3000
7000
4000 6000 8000 6000
5000 7000

5000
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7000
8000
•8138
4000
7000
5000
4000
3000
4000

PLATE I.   SKETCH MAP OF THE PHILIPPINE DEEP.

LEGEND

a Inner series of Becker
b Outer series of Becker
c Sierra Madre line

EARTHQUAKE MAP
OF THE
PHILIPPINE ISLANDS

FIGURES INDICATE SEISMIC
REGIONS, STARS APPROXIMATE
EPICENTERS
HEAVY LINES DENOTE DIRECTIONS OF
GREATEST SEISMIC INTENSITY
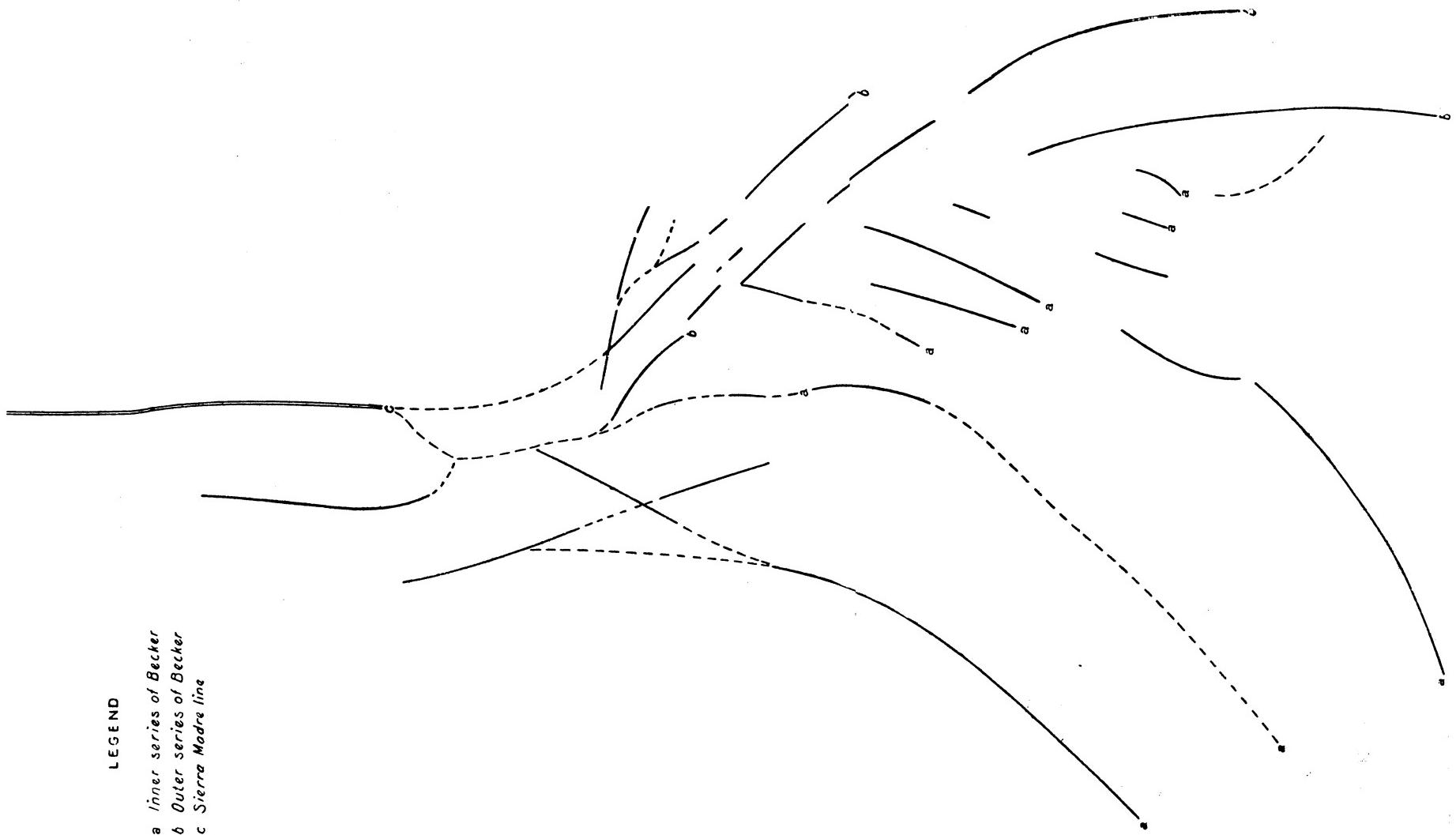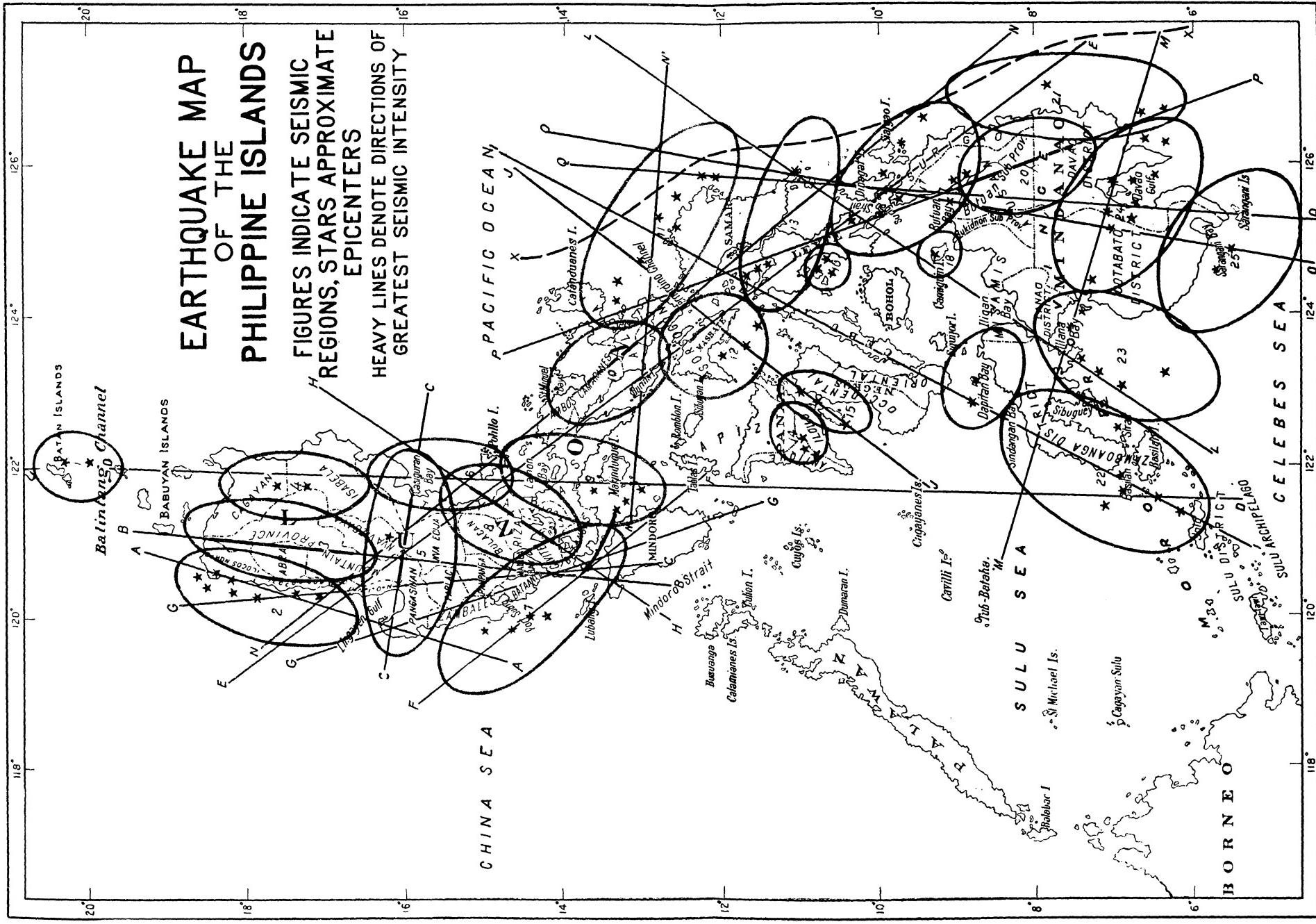
PLATE II.   EARTHQUAKE MAP OF THE PHILIPPINE ISLANDS.
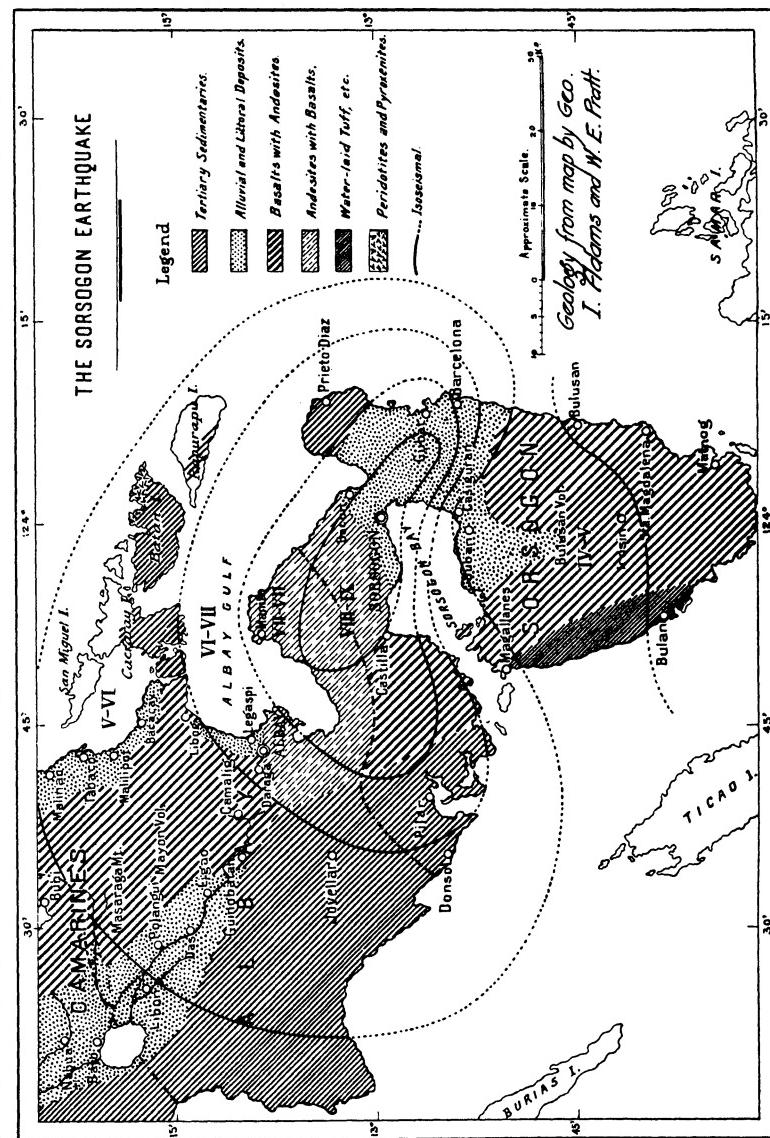
PLATE III. RELATION OF THE SORSOGON EARTHQUAKE TO THE GEOLOGY OF THAT REGION.

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CONTRIBUTIONS TO THE STRATIGRAPHY AND FOSSIL INVERTEBRATE FAUNA OF THE PHILIPPINE ISLANDS

By WARREN D. SMITH

(From the Division of Mines, Bureau of Science, Manila, P. I.)

Twenty plates

CONTENTS

INTRODUCTION

This paper is intended to serve as an introductory contribution to the large subjects of the paleontology and stratigraphy of the Philippine Islands. Much more material than is given now awaits time for the necessary studies. I have been gathering this material during eight years of exploration in the Philippine Islands when most of my time has been spent in economic work; hence, I cannot claim to have done more than open the subject. The generally poor state of petrifaction as found in those specimens which have been obtained, the limited library facilities in Manila in this particular subject, and the fact that consecutive time has not been available for study will account for some of the more or less fragmentary discussions. Twelve new species and 2 new varieties are described. It might have been expected that a larger number of new species would have been described, but where there has been the least doubt I have referred the form to a species already described. I have included generic descriptions translated from Zittel,[1] and I have omitted specific descriptions of old species. I have done this for the following reasons: For the general student in paleontology

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[1] Handbuch der Paleontologie. Munich (1876–1880), 2 and 4.

the generic description is often sufficient, and as this monograph may possibly be the basis of future paleontologic work in the University of the Philippines I have followed this procedure for the convenience of students. If more detailed information regarding the species is desired, the student can go to the original descriptions, using the references furnished in the text. Where good plates are available, descriptions are rarely needed.

The first part of this paper gives a general summary of the lithology and distribution of Philippine rocks with more detailed discussion of the Philippine sedimentary series, making comparisons with Java, particularly, and with other neighboring islands. There exists a very close similarity between the stratigraphy of the Philippines and Java, and nearly every species can be duplicated in collections from Java now deposited in the Geologisches Reichs-museum in Leiden. The same might be true of Borneo and Celebes, but geological investigations have not proceeded far enough in those islands to be of as much assistance as those that have been carried on in Java.

I have made the determinations of the species in this paper under considerable difficulties, for when the work was started there were practically no books on paleontology in Manila, and even at the present time we have only a few of the important works. The existing Spanish collections of fossils and living shells in Manila were almost useless, and there was only one fossil from the Philippines, *Vicarya callosa,* which had been figured, and that in a short preliminary brochure by K. Martin of Leiden.

In 1908 I took a portion of the Bureau of Science collection to Leiden and compared the specimens with Martin's Javan types and the Semper collection of Philippine fossils as yet undescribed. From Leiden I proceeded to London where I worked over considerable material and studied the literature in the British Museum of Natural History.

Before undertaking this work I offered several groups of fossils to different specialists in the United States to be worked up, but met with no success, these men invariably giving the excuse that they had more than they could do at home. I met with better success abroad, and Professor Douvillé of Paris has identified the greater part of our foraminiferal material, and his results have been published.[2]

Rather than delay the rest of the work longer, I have proceeded with my own limited resources with the hope that the results

[2] *This Journal, Sec. D* (1911), **6**, 53.

will have some value. My aim has been to put on record, even though it has to be revised later, what we have in the Philippines in this department of science.

I wish to make special acknowledgment of assistance rendered to Dr. K. Martin, professor of geology and head of the Geologisches Reichs-museum in Leiden; to R. Bullen-Newton, Esq., paleontologist, British Museum; to Prof. H. Douvillé, professor of paleontology in l'Ecôle de Mines, Paris; to Dr. William H. Dall, curator of conchology, United States National Museum, Washington.

PART I. STRATIGRAPHY

PHILIPPINE STRATIGRAPHY AND GENERAL STATEMENT

The same general groups of rocks exist in the Philippines as are found in other parts of the world. There are deep-seated igneous rocks, intrusives, and volcanic flows; there are metamorphic rocks and sediments, both consolidated and unconsolidated. Although the Philippine Islands may appear to the layman to be almost entirely volcanic, there is a wide distribution of the sedimentary series. In the latter the fossils are found, and consequently we can pass rapidly over the discussion of the igneous and volcanic rocks.[8]

Extrusive
- Andesites.
  - Hornblende andesite.
  - Pyroxene andesite.
  - Hornblende-pyroxene andesite.
  - Olivine-bearing pyroxene andesite.
  - Hornblende-biotite andesite.
- Basalts.
- Dacites.
- Leucite tephrites.

Plutonic and intrusive
- Granite.
- Syenite.
- Quartz diorite.
- Diorite.
- Metadiorite.
- Gabbro.
- Peroxenite.
- Peridotite.

[8] Igneous rocks of the Philippines will be found described in the following: Becker, G. F., Geology of the Philippine Islands, *21st Ann. Rept. U. S. Geol. Surv.* (1901), pt. 3, 493; Smith, W. D., The essential features of the geology of the Philippines, *This Journal, Sec. A* (1910), 5, 307; Iddings, J. P., The petrography of some igneous rocks of the Philippines, *This Journal, Sec. A* (1910), 5, 155.

Andesites and diorites are the predominant rocks in the Philippines. This will give an idea of the composition of the sediments, which, of course, have been derived largely from the erosion of these rocks.

THE SEDIMENTARY SERIES

The Philippine sedimentary formations consist of limestone, sandstone, shales, conglomerates, volcanic tuffs, and cherts.

This group includes the usual general classes to be found in any part of the world. The following list shows the order of their abundance: (1) shales and clays; (2) limestones; (3) sandstones and conglomerates; (4) tuff (waterlaid and subaërial); (5) cherts.

Besides these there are numerous subaërial deposits, piedmont deposits, etc.

Shales and clays.[4]—The shales predominate in the coal measures, varying in composition and texture from almost clay to sandstone and usually are gray, but in places they may be buff and yellow. They make up many hundred meters of thickness of strata in the Philippines. Their greatest development is in the Visayan Islands, where the most extensive coal fields also occur (Plate I).

The clays vary in composition from very impure varieties high in iron content to those which are practically pure kaolin. However, the latter are limited.

The clays of the coal measures usually contain too much free silica and not enough combined silica to be suitable for cement manufacture.

Besides the shales of the coal measures there are thin beds of shale intercalated in the great tuff series near Manila. I have found a few plant remains in these shales, and these indicate that this formation is comparatively recent. Surprisingly few plant impressions have been found in the coal measures.

Certain shale horizons show a great abundance of Foraminifera and other microscopic forms. On these I have done little work. Karrer[5] has described 27 new species of these minute organisms from the shales near Iba, Zambales, Luzon. These comprise species in the following families: Uredillæ, Milliolidæ,

[4] No attempt is made here to describe these formations in detail as the numerous geologic papers already published by this Bureau furnish these data.

[5] Karrer, Felix. Die Foraminiferen der Tertiären Thone von Luzon, appendix to Fragmente zu einer Geologie der Insel Luzon, von Drasche, R. Wien (1878).

Lagendæ, Nodosaridæ, Glandulinidæ, Frondicularidæ, Pleurosto-mellidæ, Cristellaridæ, Polymorphinidæ, Textularidæ, Globigerinidæ, Rotidæ, and Polystomellidæ. It can be seen from this then that minute forms like these are abundant. Similar shales in Cebu and on Batan Island are likewise rich in Foraminifera.

Limestones.—These are for the most part coralline or foraminiferal. They are very pure chemically, the magnesia content being generally less than 2 per cent. On Guimaras Island a slightly higher percentage has been noted in some samples. They vary in color from cream-white through buff to black. They have an extensive development, and vary in age from Oligocene to Recent.

The recently elevated limestones which are very widely distributed in the Philippines are for the most part simply raised coral reefs being largely composed of triturated and recemented coral fragments, although in places the reef has been little disturbed. Great masses of astreas, helioporas, meandrinas, turbinarias, etc., intact in the center of a mass of indurated limestone, are very common. These reefs occur at various elevations from sea level to more than 2,000 meters. The raised reefs have very much in common with those in many parts of the Pacific Ocean and China Sea region.[6] The best development of these raised reefs is along much of the Cebu coast, the coast of Ilocos Norte, in the limestone just west and north of Baguio in central Luzon, and near the north coast of Mindanao.

Becker long ago called attention to the mantle of coral limestone which must have entirely covered Cebu Island at some past time. It is possible for one to walk from the living reef fringing the shore to the highest pinnacle of the island in the Central Cordillera and, except for occasional short breaks where some stream has cut down through the mantle, to keep always on the limestone. This means that there is apparently no break between the present and the Pliocene. But this is what one would expect.

Other phases of the limestone are frequently encountered as a recemented rubble formation, well shown in the lower narrows of Danao River in Cebu.

[6] On this subject the following papers should be consulted: Newton, R. B., and Holland R., On some fossils from the Islands of Formosa and Riu-Kiu, *Journ. Coll. Sci., Imp. Univ. Tokyo* (1902), **17**, art. 6; Chapman, F., On the tertiary limestones and foraminiferal tuffs of Molekulas, New Hebrides, *Proc. Linn. Soc. N. S. W.* (1907), **32**, pt. 4; Becker, G. F., *21st Ann. Rep. U. S. Geol. Surv.*, Washington (1901), pt. 3.

The soft marly limestone of Cebu is best developed at Naga, Cebu, where good raw cement materials occur. Much the same formation is found over extensive areas of Pangasinan Province.

According to the Foraminifera these limestones and marls contain, Douvillé [7] has recognized three principal horizons, as shown in Table I.

TABLE I.—*The Philippine Tertiary.*

(After Douvillé.)

Philippines.		Borneo.	
c Upper limestone with *small* Lepidocyclines.	*Lep.* c.f. *verbeeki miogypsina.*	H Burdigalien.	Miocene.
b Sandstone and shale.	*Clycoclypeus communis, Orbitolites alveolinella, Miogypsina.*	G Aquitanien. F	
a Middle limestone with *large* Lepidocyclines.	*Lep. insulae-natalis, formosa, richthofeni.*	E	
Lower limestone with Numulites, coal measures.	*Nummulites niasi Verb., Amphistegina* c.f. *niasi, Lepidocyclina.*	D Stampien.	Upper Oligocene.

In an article on coal-mining operations on Batan Island in the early days of the American occupation, Reinholt [8] writes as follows:

The sedimentary series belong unquestionably to the Tertiary Period. Professor Mayer of Zürich and Doctor Dall of our Smithsonian Institution, agree, from the examination of fossils collected and personally submitted by me, that the upper limestone should be referred to the Oligocene epoch.[9]

This does not agree exactly with Douvillé's findings which were based on the Foraminifera. I have collected *Ampullinopsis* on Batan Island, but from the *lower* limestone.

Sandstones and conglomerates.—In the coal measures there are several small seams which may be called grit. Sometimes the quartz fragments in this grit are over 2 centimeters in diameter. In addition there is at least one thick stratum of a very impure, grayish sandstone overlying the uppermost coal seams in most parts of the Islands, and this is particularly well developed in Cebu. This formation more properly should be called an arkose rather than a sandstone, because it contains more feldspathic, hornblendic, etc. material. There is very little pure quartz sandstone in the Archipelago.

The conglomerates are of two classes—basal and subaërial.

The greatest development of conglomerate in the Islands is that bordering the igneous complex of north-central Luzon, as

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[7] *This Journal, Sec. D* (1911), **6**, 77.

[8] *Eng. Mag.* (1906), **30**, 510.

[9] "The presence of Ampullinopsis among the shells is indicative of this age."—Letter from Dr. Wm. H. Dall. [Footnote in the original.]

is seen in sections along the Bued and Agno Rivers. This is basal. Other great deposits of conglomerate are encountered farther north at an elevation of nearly 2,000 meters. In some localities this formation is fairly rich in fossils, as in Trinidad Gap, Benguet.

Probably the best geological sections in the Archipelago are on Panay. These show great thicknesses of conglomerate and sandstone. The conglomerates here are bedded and conformable to the strata above and below.

Tuffs.—There is a great deposit of pyroclastic material, with intercalated beds of sand and silt extending over a considerable area of southwestern Luzon, particularly over Cavite and Batangas Provinces and the country adjacent to Manila. A great deal of this material probably came from Taal Volcano, but also from other vents, many of which in a former period existed throughout this region. When first quarried, the material is soft, but gradually hardens on exposure. It is buff to gray in color. It was extensively used in the Spanish régime, and is still quarried to a less extent for building purposes. This stone is known in the trade as "Guadalupe stone." Fragments of pumice, black hornblendes, fragments of feldspar, etc. give the rock a very heterogeneous composition and coarse texture. The maximum thickness of the deposit is probably more than 100 meters. The best exposures are to be seen in several quarries along the banks of the Pasig River. This deposit has yielded a few fossils.

Adams,[10] who has studied this tuff more closely perhaps than any one else, says of these fossils:

Occasionally a log of wood has been encountered in drilling, and plant remains, fish teeth (fig. 3), and one mammalian tooth (fig. 4) have been found in the beds. The presence of the plant remains has been recorded by many observers. The greatest depth at which a log of wood has been found is in the Alabang wells southeast of Manila where one was cut by the drill at a depth of between 130 and 132 meters. The mammalian tooth was obtained from the Pasig well at a depth somewhere between 81 and 85 meters. [Figs. 3 and 4 refer to Adams's article.]

[10] *This Journal, Sec. A* (1910), **5**, 73.

TABLE II.—*Provisional table of Philippine stratigraphy.*

Period.	Formation.	Name.	Type locality.	Distribution.	Economic deposit.	Characteristic fossil.
	Piedmont deposits		Pangasinan	General	Gravel	
	Fluviatile deposits:					
	High level		Cagayan, Mindanao	General	Bench placers—gold	
	Lower level		Paracale, Luzon	do	Deep placers—gold and platinum.	
	Spring deposits		Mountain Province	Central Luzon	Salt and silica	
	Talus deposits		do	General		
Recent	Littoral deposits		Sangley Point	do	Building sand	
	Coral reefs			do	Building stone and lime.	
	Pyroclastic deposits a	"Guadalupe stone"	Pasig River	Rizal, Laguna, and Batangas Provinces.	Building stone	Leaves of Euphorbiaceæ (?) deer's and sharks' teeth.
	Raised coral reefs a		Coast of Ilocos Norte	Many parts of west coast.	Lime	
	Marine conglomerates a		El Fraile Island	Manila Bay		
Unconformity (not marked).	Basalt and andesitic flows and ejecta. a		Mount Arayat / Mount Apo	Southern Luzon and Mindanao.	Road metal	
	Raised coral reefs		Cebu, west coast	Many parts of Archipelago.		
Pleistocene and Pliocene.	Marls	Laoag	Ilocos Norte	Many parts of the Islands. Well developed. Agusan Valley, Mindanao.		*Hindsia dijka* Mart.
	Eruptives		Mount Mariveles	Luzon, Panay, Mindanao, etc.	Construction material, road metal.	

	Formation		Locality	Distribution	Economic use	Remarks
Unconformity.	Limestone (upper)	Licos	Cebu	Cebu, northern Luzon, Panay.	Burned for lime	Small lepidocyclines. Shells very similar to recent forms; corals abundant. *Orbitolites martini.*
Miocene	Marl	Alpaco	do	Cebu and Luzon		
	Iron formation?	Hizon	Bulacan, Luzon	Eastern Luzon	Iron	
	Intrusive andesite and diorite, quartz diorites dacites.		Cebu	Cebu, Luzon, Masbate.	Gold, silver, manganese, lead, copper, road metal.	
Unconformity	Quartz porphyry b	Mancayan	Lepanto	Luzon	Copper	
	Granite and granite gneiss. b		Camarines	Luzon	Gold	
	Crystalline schists b	Zamboanga	Mindanao	Mindanao and Luzon	do	
	Middle limestone	Binangonan	Luzon	Luzon, Cebu, etc	For construction material.	Large lepidocyclines. *Lepidocyclina richthofeni. Lithothamnium,* etc.
Miocene	Sandstone with conglomeratic phases.	Suague	Panay	Throughout the Archipelago.	Abrasives	
	Shale (Two facies probably contemporaneous.)	(a) Batan	Batan Island	Throughout the Visayan Islands, Luzon, and Mindanao.	Coal	*Vicarya callosa* and *Callianassa dijki.*
		(b) Vigo	Tayabas Peninsula	Luzon, Cebu, Leyte	Light oil	
Oligocene *Unconformity.*	Lower limestone.	Camansi	Cebu	Batan, Cebu, etc		*Nummulites niasi.*
Pre-Tertiary, Jurassic (?)	Cherts	Baruyen	Ilocos Norte	Luzon, Palawan, etc		Radiolaria and sponge spicules.
	"Slates"	Ulion	Panay	Luzon, Panay, Palawan.		Radiolaria: *Cenosphaera* and *Dictyomitra.*

a Or late Pleistocene. b Doubt as to true position.

TABLE II.—*Provisional table of Philippine stratigraphy—Continued.*

Period.	Formation.	Name.	Type locality.	Distribution.	Economic deposit.	Characteristic fossil.
Unconformity	Basal conglomerate	Agno	Luzon	General		
	Syenites[a]	Aroroy	Masbate			
	Diorites	Benguet	Luzon	Luzon, Cebu, Palawan, etc.	Gold	
Igneous complex, age uncertain.	Gabbros	Malirong	Leyte	Leyte and Luzon		
	Pyroxenites	Cinco Picos	Bataan	Luzon and Mindanao	Asbestos	
	Perioditites	Subic	do	Luzon and Panay		

[a] Or late Pleistocene.

Cherts.—In Ilocos Norte, Pangasinan, Balabac, Panay, and other localities there are outcrops of hard, red cherts or jaspers, in some places as hard structureless bowlders, and in others as fissile beds.   When I first found these in Ilocos Norte, I compared them with the cherts of California.[11]   On examination with a microscope they were found to contain fragments of radiolarian tests.   These rocks have a wide distribution in this part of the world, and have been provisionally assigned to the Jurassic by Martin.[12]

Table II is a provisional table of Philippine stratigraphy revised from similar ones which have appeared in my earlier papers.   This gives the vertical distribution, as near as we now know it, of the various sedimentary formations and their relations to the different igneous rocks.

It is my opinion that while some of the coal measures belong to the Eocene, most of the coal seams occur in the Miocene, particularly the uppermost and the poorer seams such as the East Batan.

Old "slates" and other rocks.—Masses of indurated sediments almost slaty in character are found in certain islands and are pretty certainly older than the Tertiary.

Abella called attention to these in Misamis, Mindanao, and near O'Donnell, Luzon.[13]

In a report made in 1900, Becker [14] wrote as follows:

* * * If such strata exist, it may be that they are so folded up with the greatly disturbed Eocene that they have not hitherto been differentiated.   From the descriptions of Surigao and Misamis, it would seem, too, that considerable areas of slate are there exposed and that portions of these rocks are not highly metamorphosed.   This region may possibly yield fossils.   In carrying on geological investigations in the Philippine Islands, the indications afforded by the constitution of neighboring islands should evidently be borne in mind, for if the similarities which might be expected do not manifest themselves, the cause of difference demands elucidation.

Ferguson [15] describes from the Island of Masbate a series of slate-like rocks on Kaal Creek.   Some of these slate rocks are reddish, containing psilomelane lenses; other portions are darker and invariably lined with a minute network of quartz and calcite veins.

[11] *This Journal, Sec. A* (1907), 2, 235–253.
[12] Reisen in den Molukken.   Leiden (1903), pt. 3.
[13] Manantiales Minerales de Filipinas.   Manila (1893), 144.
[14] *Op. cit.*, 547.
[15] *This Journal, Sec. A* (1911), 6, 404, 405.

He says:

Little can be said as to the absolute age of the Kaal formation. No fossils have been found, but judging from its position, its extreme contortion and considerable metamorphism, it is my belief that it may be classed provisionally as pre-Tertiary, * * *.

My own comment at the time was:

Metamorphism is no longer considered an indication of age; Tertiary rocks have been subjected to profound dynamic stresses and are metamorphosed. Without fossils the question can not be satisfactorily settled.

I am still of this opinion with regard to this particular formation.

On the Island of Panay there is a series of much indurated sediments which is quite distinct from the later sediments known certainly to be Tertiary. These were encountered in the upper reaches of the Ulian River almost in the heart of the cordillera. Their position, lithology, strike, and dip all preclude the possibility of their belonging to the younger series. In fact, an intervening basal conglomerate makes this practically a certainty.

This formation for the most part consists of very hard, fine-grained material with fairly well-developed slaty cleavage. In the same region, but not exactly associated with these beds, are some red and green beds which have proved to be cherts and serpentines. In these we found on microscopic examination of thin sections some structures similar to those seen in the Ilocos Norte cherts.

Mr. Dalburg, formerly of this Bureau, recently brought from Bulacan Province, Luzon, rocks similar to those found in Panay. Slide preparations of these rocks revealed excellent sections of radiolarian tests of *Cenosphæra affinis* Hinde and *Dictyomitra tenuis* Hinde.

Similar forms have been described by Hinde[16] in rocks collected in central Borneo by Molengraaff. From his description of these cherts and diabase tuffs I am more than ever inclined to the opinion expressed in 1905[17] that these formations are Mesozoic and that they are equivalent to those of the Moluccas, Borneo, etc.

The crystalline schists.—The crystalline schists are, in my opinion, in part at least, of Tertiary age, and, as far as I can tell from field evidence, they are in some places, at least, metamorphosed Tertiary sandstones and shales. However, in

[16] Hinde, Appendix to Molengraaff's Borneo. Amsterdam (1899).
[17] *This Journal*, Sec. A (1907), 2, 145.

northern Mindanao, in Surigao Peninsula particularly, there is a metamorphic area consisting of argillo-arenaceous and micaceous schists with quartz stringers. These may possibly be older than the Tertiary, but there is no fossil evidence nor has any satisfactory field evidence been brought forward to show that they lie below the Tertiary series, although similar schists are found in that position in Java. We may yet find the same to be the case here.

Distribution.—The general statement may be made that the oldest rocks probably are those found in the deep cañons of the cordilleras of Luzon. In many other parts of the Islands where we might hope to find them we encounter everything covered by a sheet of volcanic rocks, as is the case with much of the western part of Mindanao, or else by a mantle of coral limestone, as in Cebu. Flanking these older rocks, and dipping away from them both to the east and west, are the Tertiary sediments, limestone, sandstone, shale, and the intercalated coal seams; above these are andesites and basaltic flows, while the youngest consolidated formation of all is the tuff of the vicinity of Manila. It is not easy in our present state of knowledge to delimit all of these formations; indeed, many which appear to be of different age are, in reality, contemporaneous. Another noteworthy fact is particularly well exemplified in Cebu, namely, that there is no apparent break in the limestone from the coral reef on the shore to the capping of the cordillera in the center of the island, at a height of 1,000 meters. It probably sank below sea level and subsequently rose so gradually that the whole island was covered with a mantle of coral. This mantle has since largely been removed by erosion. The map (Plate I), showing the general distribution of the various formations throughout the Archipelago, was prepared in this Bureau from data from various sources, but mainly from our own surveys.

COMPARISON WITH JAVA

Martin [18] in his paper concerning Tertiary fossils in the Philippines which was translated by Becker as a complement to his report on the geology of the Philippines, called attention to the strong resemblance of the fauna of the Philippines to that of Java based on his examination of the Semper collection now in the Reichs-museum in Leiden. The Semper collection contains the following fossils already determined:

[18] *Samm. d. geol. Reichs-mus. in Leiden* (1896), **5**, 53–69.

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Martin's list (1896).

Species.	Age in other parts of this region.
Terebra jenkinsi K. Mart.	M.
Terebra bandongensis K. Mart.	M.
Conus sinensis Sow.	P. L.
Conus insculptus Kien.	M L.
Conus palabuanensis K. Mart.	J.
Conus loroisii Kien.	M. P. L.
Pleurotoma gendinganensis K. Mart.	P.
Pleurotoma carinata Gray.	P. L.
Pleurotoma coronifera K. Mart.	E. ?; M.
Pleurotoma neglecta K. Mart.	M.
Turricula bataviana K. Mart.	P.
Fusus verbeeki K. Mart.	M. P.
Latirus madiunensis K. Mart.	P.
Pyrula gigas K. Mart.	M.
Tritonidea ventriosa K. Mart.	M.
Nassa verbeeki K. Mart.	P.
Murex verbeeki K. Mart.	P.
Murex djarianensis K. Mart.	M.
Murex brevispina Lam.	M. ?; P. L.
Murex pinnatus Wood.	M. L.
Murex microphyllus Lam.	M. L.
Murex capucinus Lam.	– L.
Murex grooti Jenk.	M.
Ranella spinosa Lam.	M. L.
Ranella elegans Beck.	M. L.
Ranella raninoides K. Mart.	M.
Ranella gyrina Linn.	– L.
Cypraea smithi K. Mart.	M.
Strombus isabella Lam.	Q. L.
Rostellarea javana K. Mart.	M.
Vicarya callosa Jenk.	M.
Potamides jenkinsi K. Mart.	P.
Turritella terebra Lam.	Q. L.
Natica mamilla Lam.	M. L.
Arca granosa Linn.	P. L.
Cardita decipiens K. Mart.	P.
Venus squamosa Lam.	P. L.
Clementia papyracea Gray.	M. P. L.
Corbula scaphoides Hinds.	M. P. L.
Callianassa dyki K. Mart.	M. Q.

E denotes Eocene; M, Miocene; P, Pliocene; J, later Tertiary in general; Q, Quaternary; L, living species.

Only one of these, *Vicarya callosa*, has been figured.

Martin calls particular attention to *Vicarya callosa* Jenk. (Plate VI, figs. 4 to 7). It is indeed the most characteristic fossil in the Philippine Tertiary invertebrate fauna, and is a most important zone fossil. Wherever it has been found so far, it occurs in the gray shale just above the coal seams. Investi-

gators of Philippine coal deposits will find this form most useful for purposes of correlation.

The following stratigraphic column from Verbeek and Fennema [19] can be seen at a glance to duplicate the Philippine sequence of formations in many items almost exactly.

Stratigraphy of Java.

(Beginning at the bottom.)

I. Argillaceous schists, quartzites with quartz veins, without petrifaction (schists of the Carimuon diawa)..Age ?

II. Schists with serpentine, mica, chlorite, and argillaceous material, quartzites, some calcareous beds and interposed sills of eruptive rocks, diabase, gabbro, quartz porphyry..............................Cretaceous.

III. Gray quartzose argillites with beds of coals, breccias of diabase, quartz, etc., conglomerates of quartz and granite, marls with alveolines and limestone with nummulites......Lower Tertiary or Eocene.

IV. Eruptive rocks in the preceding stage, the oldest andesites, with the characters of diorites and diabase......Lower Tertiary, Eocene.

V. Terrane of Nanggoulan..Oligocene.

VI. Eruptive rocks at the base of the Miocene.

VII. The Lower stage of the Upper Tertiary, called the "Breccia Stage," composed of breccia of eruptive Tertiary rocks with grits, shales, with some marl and beds of limestone....................Lower Miocene.

VIII. Eruptive rocks of the preceding stage............................Lower Miocene.

IX. The middle stage for the Upper Tertiary, called the "Marly Stage," containing much marl and marly sandstones, but less of sandstone and shales; some calcareous beds. Middle Miocene with the uppermost beds in part Pliocene.

X. Eruptive rocks of the preceding stage........Middle and upper Miocene.

XI. The most recent stage of the Upper Tertiary called the "Calcareous Stage;" much limestone and marly limestones alternating with marl...Upper Miocene and Pliocene.

XII. Recent volcanic rocks; volcanoes. Miocene, Pliocene, Quaternary, and Recent.

XIII. Old post-Tertiary sediments with some fossil mammals....Quaternary.

XIV. Recent post-Tertiary sediments..Recent.

If we examine each of these formations in turn, we can see considerable similarity to the formations of the Philippines.

No. I can be duplicated almost exactly in various parts of northern and southern Mindanao, at Placer in Misamis, and on the Zamboanga Peninsula.

No. II can be duplicated on Palawan Island. However, I am loath to believe that these rocks are Mesozoic without more evidence.

No. III is exactly what we find on Batan and Cebu Islands.

No. IV we have in Benguet, Cebu, and in various other parts of

[19] Verbeek, R. D. M., and Fennema, R., Description Géologique de Java et Madoura. Amsterdam (1896), 38.

the Philippines. The older andesite in Benguet can scarcely be distinguished from diorite, and grades into it.

We have at Alpaco near Naga, Cebu, a marl which corresponds very closely to No. V in this table, and is most certainly Oligocene.

In Cebu Island there are eruptive rocks at the base of the Miocene, principally andesites, which correspond to No. VI.

There are volcanic breccias in the Philippines, some of which correspond to No. VII. The volcanic breccia in northern and central Luzon, particularly well developed around Baguio, is, in part, of this formation.

The marly limestone of the Danao district, Cebu, is probably equivalent to No. IX of this table.

Undoubtedly much of the eruptive rock of the Philippines should be referred to the same stage as represented by No. X in this table; that is, middle and upper Miocene. Diorite intrusions have been found in Benguet cutting Miocene limestone.

The upper Miocene and Pliocene "Calcareous Stage" shown in No. XI can be exactly duplicated in the Philippines; it is particularly well developed in Cebu where many of the fossils illustrated in this paper were collected. This formation is characterized by the foraminifer, *Lepidocyclina,* and by the marine alga, *Lithothamnium.*

No. XII can be duplicated at many points in the Philippines.

No. XIII is represented in the Philippines by Pleistocene deposits in the Agusan Valley, Mindanao, the great tuff deposits around Manila, etc. A few fossil teeth of mammals have been found in the latter formation.

No. XIV is represented in the Philippines.

FOSSIL LOCALITIES

The principal fossil localities (Plate II) in the Philippines are as follows:

1. Liguan, Batan Island, Albay Province, Luzon. This locality contains shale, sandstone, and limestone, but No. 1 refers to the hard, bluish to buff limestone, occurring near the military mine.
2. Caracaran River, Batan Island; hard, bluish to buff limestone, probably the same as No. 1.
3. Sitio of Manila, Batan Island; limestone. This formation contains numerous specimens of *Ampullinopsis,* a form which is referred by Dall to the Oligocene.
4. Calanaga Bay, Batan Island; marl and limestone alternating in thin beds, dipping at various angles from 20° to 45° to the north. They are grayish to yellow and contain numerous Foraminifera.

5. Moncao Bay, Batan Island; just north of this bed is a considerable series of limestones and shales.
6. Bilbao, Batan Island; thin grayish shale overlying lignite seams.
7. Batan, Batan Island; gray shale overlying the East Batan coal seam; contains *Vicarya callosa*, etc. and numerous species of *Corbula*.
8. Gaba Bay, Batan Island; grayish marl something like No. 4.
9. Agundi, Batan Island; coast limestone.
10. Caracaran River, Batan Island; thin-bedded shales, alternating with limestone beds. These probably belong to the Miocene and overlie the principal coal beds.
11. Nagtagan Island near Batan; limestone which is the same formation as that which occurs on the west end of Batan Island.
12. San Ramon Point, Batan Island; shale.
13. White to cream-colored upper limestone near Dapdap, Batan Island.
20. Loboo River, Batangas Province, where the trail crosses to the Loboo Mountains. This is a dark grayish coarse indurated shale with bowlders in it. It is very hard and difficult to pick. This probably belongs to the Miocene. In 1905 I visited this locality and was of the opinion that this shale immediately overlay the basal conglomerate from the bowlders which occurred in it. Subsequent experience in the Philippines necessitates a modification of my former conclusion. This formation may not be very near the basal conglomerate. In fact, the whole lower Miocene and Eocene may be deeply buried at this point. Therefore, the statement, made at that time, that coal would probably not be found underlying this shale, ought to be omitted.
21. From a cream-colored limestone overlying the above formation in the same locality as No. 20.
22. Limestone at Point Ilihan on the Batangas coast; not visited by me; probably Pliocene. Collected by C. M. Weber.
23. Point Buri, Batangas coast; limestone. Collected by C. M. Weber.
24. Ilaga Creek, Batangas; Miocene limestone like No. 21.
41. Baguio, Benguet, 1 kilometer west of the city hall. This is a reddish sandstone, very friable, which is very rich in fossil clam shells. The peculiar heterogeneous composition and reddish color of this sandstone is due to the fact that it is made up of detritus from volcanic rocks upon which it rests. It is more in the nature of an arkose. This is probably Miocene.
42. Benguet Road, Mountain Province, Luzon, on the zigzag just below McElroy's old camp. This is a coal-black limestone containing numerous bivalves. The black color is due probably to impurities at the time of formation of this deposit.
43. Trinidad Water Gap at the southern entrance to Trinidad Valley. There is a basal conglomerate which outcrops just below the limestone on the trail just at the entrance to the gap. It is rich in the same kinds of fossils as are found at locality 41.
44. Trinidad Water Gap, across the stream on the northeast side of the river. This is a coral reef which contains numerous coral fragments of species still living in the China Sea. It is now about 1,500 meters above sea level.

45. Limestone ridge 2 kilometers west of the city hall and north of the observatory, Baguio, Benguet. This bluish to white limestone is very rich in poorly preserved fossils; the characteristic species is *Turbo borneënsis*. It is probably upper Miocene or early Pliocene. This is the uppermost limestone in the Benguet district.

46. Benguet Road, Mountain Province, Luzon; 2 kilometers above Twin Peaks. This is a very hard, light- to brown-colored formation; probably Miocene at this point.

272. On south slope of Mount Mangilao near Danao. This locality is at the base of the upper limestone and at the summit of a lower limestone horizon. There is a marl below this which is apparently unfossiliferous. The fossils were picked up where they had already weathered out of the formation; elevation about 200 meters above sea level.

273. This is a yellow marl found in Sibod Gulch, Naga, Cebu; probably Miocene.

274. Talamban near Panopoy; upper limestone, white and irregular.

275. Opan on Mactan Island, Cebu; Recent raised coral limestone.

276. An upper coral bed on Mactan near Cebu.

277. Soft white chalky limestone cliffs on the Minanga River, Cebu, Toledo Road near Camp One. This is probably Pliocene limestone.

278. Hard buff-colored limestone above the coal seams at Guilaguila, Cebu; contains numerous Foraminifera.

279. Cotabato Valley near Mount Uling, Cebu; limestone.

280. Malbog, Alegria, Cebu; Pliocene limestone.

281. Limestone near oil horizon, 500 meters above sea level, Alegria, Cebu.

282. Mangilao; white limestone just above coal at Carmen, Cebu.

283. On the road between San Fernando and Naga, Cebu; float specimen.

284. Limestone; specimen given me by a native woman in Toledo, Cebu; locality unknown.

285. Cumajumayan Hill; Cebu. No limestone on top of this hill, but the fossils are from a limestone formation which has since been removed.

286. Upper limestone, Lantauan Ridge, Cebu. This contains the characteristic alga *Lithothamnium*.

287. Travertine; in the stream in Cumajumayan Valley, Cebu.

288. Cabecelino Creek, Cebu.

289. Shale beds above the coal at Compostela, Cebu.

293. Cream-colored rather open limestone; Cotabato Hill, Mindanao. This limestone is rich in fossils which are upper Miocene or Pliocene.

356. Cut in the road between Laoag and Bacarra, Ilocos Norte, Luzon. Unconsolidated gray to white sandy marl; fossils in some cases retain original color; very rich in perfectly preserved shells; deposit is undoubtedly Recent.

609. On the beach, northeast coast of Semirara Island. Fossils evidently weathered out of limestone. Collected by H. D. McCaskey.

778. Cave near the beach at Puerto Princesa; recent limestone. Collections by C. M. Weber.

TABLE III.—*Tentative correlation of the Far Eastern Tertiary.*[a]

Series.	Philippines.	Borneo.	Java.	Formosa.	Japan.	New Hebrides.	India.	Europe.
Pliocene	Raised coral reef limestone		Limestone	Raised coral reef limestone	Marine beds with *Mytilus, Conchoccle*	Limestone with *Sphæroidina dehiscens.*		Astian.
Do	do							Plaisancian.
Pre-Pliocene	Limestone and marl beds. Fossil elephants' teeth reported from two localities in Luzon and one in Mindanao. Foraminiferal marls of Karrer probably belong here also.		Etage calcareux		Beds containing fossil plants and those containing numerous specimens of *Carcharodon megaladon.*	Foraminiferal limestone and tuffs with andesitic sills.	Manchar siwaliks (vertebrate fossils)	Pontian.
Miocene: Upper	Upper limestone, with small Lepidocyclines. Limestones with *Cycloclypeus.*	Group H with small Lepidocyclines and *Lithothamnium.*	Limestones with *small* Lepidocyclines. Volcanic tuff and sands, with *Cycloclypeus.* Limestones with Lepidocyclines and *Cycloclypeus.*	Limestones with Lepidocyclines and *Lithothamnium.*	Limestones with Lepidocyclines, *Lithothamnium.*	Limestones with *Lithothamnium.* Foraminiferal tuffs.		Burdigalian.
Middle	Sandstones and shales with *Vicarya callosa.* Coal seams.		Sandstones	Sandstone, shale, coal seams	Sandstone; shales; coal seams with *Vicarya callosa* in the overlying beds.		Gaj. Arenaceous group. *Vicarya verneuili, Ostrea multicostata.*	Aquitanian.
Lower	Middle limestone, with large Lepidocyclines	Group G	Etage brecheux				Argillaceous group	
Oligocene	Lower limestone with *Nummulites.* Coal seams.	Group D and C with *Nummulites.*	Limestones with *Nummulites*				Nari formation with *Orbitoides papyracea.*	Ruxelian. grian.
Eocene	Some coal seams. Exact position doubtful.	Group B with *Operculina.* Group A with *Orthophragmina omphalus.*	Quartzose argillites with coal seams.		Tuffs with *Nummulites* (Bonin series).		Kirthar with *Nummulites* and *Alveolina.*	Bartonian. Lutetian.
Paleocene	Uncertain				Sandstone, shales, coal seams		Ranikot	Suessonian. Thanetian. Montian.

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[a] The authorities drawn upon for this table are: Becker, Koto, Verbeek, Martin, Douvillé, Chapman, Oldham, De Lapparent, Fukutome, Inouye, and Smith.

822. This is the classic locality of Binangonan, Luzon, where von Richthofen collected *"Nummulites,"* but which have been found to be *Orbitoides.* This is a limestone ridge surrounded by a basalt flow about 7 kilometers from Laguna de Bay.

823. Limestone cave about 8 kilometers east of Antipolo, Luzon. This is the upper Miocene or Pliocene limestone and is the same formation as the Binangonan limestone.

907. West side of Aroroy, near Colorado Point, Masbate. Gray sandy shale; Miocene.

1034. Tumaga River about 10 kilometers north of Zamboanga Peninsula, Mindanao. Miocene shale. *Vicarya callosa* was found here, indicating a possible occurrence of coal seams below.

1054. San Rafael, Agusan River, Mindanao; recent sandy shale deposit. Collected by M. Goodman.

1055. Agusan River; exact location not given. Collected by M. Goodman.

1056. Agusan River; all recent shale deposits. Collected by M. Goodman.

CORRELATION OVER THE FAR EAST

The relationship between the stratigraphy of the Philippines and the rest of the Oriental Region is shown by Table III which will speak more convincingly than many pages of comment.

CONCLUSIONS

1. As far as we know all Philippine fossils except some radiolarian tests are Tertiary and Recent.

2. The oldest fossils we know definitely at present are certain radiolarian species which are almost certainly Jurassic.

3. Philippine fossils are as a rule poorly preserved, and we have so far found very few new species.

4. The Philippine fauna does not differ essentially from that of Java.

5. Tertiary conditions still exist in portions of the Archipelago.

6. The mica and chlorite schists may be Tertiary and are not necessarily ancient.

PART II.   PALEONTOLOGY

LIST OF SPECIES

Conidæ.
  Conus sulcatus var. *philippinensis* var. nov.
  Conus odengensis K. Mart.
  Conus djarianensis K. Mart.
  Conus sp.
Fusidæ.
  Turbinella ilocana sp. nov.
  Turbinella (Fusus) tjidamarensis K. Mart.

Fusidæ—Continued.
  Tritonidea (Pollia) ventriosa K. Mart.
Buccinidæ.
  Hindsia dijki K. Mart.
Volutidæ.
  Voluta sp. indet.
  Turricula jonkeri K. Mart.
  Turricula bataviana K. Mart.

Pleurotomidæ.
  Turris (*Pleurotoma*) *andaënsis* sp. nov.
  Turris (*Pleurotoma*) *carinata* Gray.
  Turris (*Pleurotoma*) *flavidula* Lam. var. *sonde* K. Mart.
  Turris (?) *agusana* sp. nov.
Nassidæ.
  Nassa caniculata Lam.
  Nassa verbeeki K. Mart.
  Nassa siquijorensis A. Adams.
Strombidæ.
  Rimella javana K. Mart.
Cassidæ.
  Cassidaria echinophora Linn. (?)
  Cassis pila Reeve.
  Cassis nodulosa Gmel.
Doliidæ.
  Pyrula (*Melongena*) sp.
  Dolium costatum Menke.
Melaniidæ.
  Melania laterita Lea.
  Melania woodwardi K. Mart.
Naticidæ.
  Natica globosa Chem.
  Natica marochiensis Gmel.
  Natica rostalina Jenk. (?)
  Natica (*Lunatia*) sp.
  Polynices (*Natica*) *mamilla* Lam.
Tritonidæ.
  Bursa (*Ranella*) *subgranosa* Beck.
Turritellidæ.
  Turritella terebra Lam.
  Turritella cingulifera Sow.
Cerithiidæ.
  Vicarya callosa Jenk. var. *semperi* Smith.
  Cerithium (*Campanile*) sp.
  Cerithium (*Potamides*) *palustris* Linn.
Solenidæ.
  Azor coarctatus Gm.
  Cultellus maximus Gm.
Mytilidæ.
  Modiolus sp.
  Clementia sp.
  Clementia papyracea Gray.

Veneridæ.
  Macrocallista ventricola K. Mart. (?)
  Chione (*Venus*) *chlorotica* Phil.
  Chione (*Venus*) *pulcherrima* K. Mart.
  Dosinia boettgeri K. Mart.
Pectinidæ.
  Pecten pallium Linn.
  Pecten sulcatus Müll.
  Pecten senatorius Gmel.
  Chlamys (*Æquipecten*) (?) sp. indet.
Spondylidæ.
  Spondylus sp.
  Spondylus ducalis Chem. (?)
  Plicatula imbricata Menke.
Lucinidæ.
  Lucina (*Codakia*) sp.
Cardiidæ.
  Cardium elongatum Brug.
  Cardium flavum Linn. (?)
Arcidæ.
  Arca nodosa K. Mart. (?)
Parallelodontidæ.
  Cucullaea holoserica Reeve (?)
Astartidæ.
  Cardita boettgeri K. Mart.
Tridacnidæ.
  Tridacna gigas Lam.
Ostreidæ.
  Ostrea sp.
  Alectryonia folium Linn.
Corallinaceæ.
  Lithothamnium ramosissimum Reuss.
Radiolaria.
  Cenosphæra affinis Hinde.
  Dictyomitra tenuis Hinde.
Nummulinidæ.
  Operculina costata d'Orb.
  Orbitolites complanata Lam. (?)
  Lepidocyclina insulæ-natalis Jones et Chap.
  Lepidocyclina formosa Schlumb. (?)
Lithophylliaceæ.
  Montlivaultia bulacana sp. nov.
  Montlivaultia robusta sp. nov.
  Montlivaultia cortada sp. nov.
  Pattalophyllia (?) *bonita* sp. nov.

Lithophylliaceæ—Continued.
  Caryophyllia (?) *laoagana* sp.
    nov.
  Flabellum australe Moseley (?)
  Odontocyathus coloradus sp. nov.
Lophoserinæ.
  Cycloseris decipiens K. Mart.
  Pachyseris cristata K. Mart. (?)
  Ptychocyathus (?) *incognitus*
    sp. nov.
Lithistidæ.
  Chenendopora (?) *major* sp.
    nov.

Madreporidæ.
  Madrepora duncani Reuss (?)
Astreaceæ.
  Prionastraea (?) *vasta* Klz.
Spatangidæ.
  Schizaster subrhomboidalis
    Herkl.
Solenoconchæ.
  Dentalium tumidum sp. nov.
Vermetidæ.
  Vermetus giganteus K. Mart.
Thalassinidæ.
  Callianassa dijki K. Mart.

DESCRIPTION OF SPECIES

GASTEROPODA

CONIDÆ

CONUS Linnæus

Shell convolute, inverted, top shaped, sometimes quite cylindrical, spire short, conical; mouth long, narrow, without teeth or wrinkles, possessing anterior outlet; outer lip sharp, plain, sometimes with a gap posteriorly; operculum horny, narrow. *Conus* includes 526 recent and about 160 fossil species, principally distributed in the younger Tertiary formations. (*Zittel.*)

The genus *Conus* reaches its greatest development in the tropics, and the most valued living species, *C. gloria-maris* Hwass, was found in the Philippines. They are beach forms. This fact indicates that the formations containing fossils of this genus were laid down in shallow water.

Species of Conus found fossil in the Philippines.

Conus sinensis Sow. Semper collection (Leiden).
    (Çonch. Ill., fig. 56.)
Conus insculptus Kien. Semper collection.
    (Icon. Coq. Viv., Pl. 99, fig. 2.)
Conus palembuanensis K. Mart. Semper collection.
    (Foss. v. Java, Pl. II, fig. 26.)
Conus loroisii Kien. Semper collection.
    (Foss. v. Java, Pl. III, fig. 52.)
Conus acutangulus Chem. (?) Bureau of Science collection.
Conus odengensis K. Mart. Bureau of Science collection.
Conus sulcatus Hwass var. *philippinensis* var. nov. Bureau of Science collection.
Conus vimineus Reeve. Bureau of Science collection.
Conus hardi (?) Bureau of Science collection.
Çonus djarianensis K. Mart. Bureau of Science collection.
Conus parvulus K. Mart. Bureau of Science collection.

Conus sulcatus Hwass var. philippinensis var. nov. Plate II, fig. 1.

Tryon, Man. Conchol. 6, Pl. 23, figs. 79a–81;

K. Martin, Foss. v. Java, 1, n. s., Pl. I, figs. 11 and 12.

This is a very fresh looking and well preserved shell, 5 centimeters high and 2.5 centimeters wide.   It is very closely related to both *C. sulcatus* Hwass, still living in Philippine waters, and to the variety *sonde* described by Martin from Java.   The form figured here has only 1 fine thread-like ridge in the main sulcations instead of 2 or more as in the other varieties.   This difference seems scarcely important enough to warrant even a varietal name, but one is given to show that there is a slight difference.

Locality: Punta Colorada, Aroroy, Masbate, No. 907.[20]

Formation: Pliocene (?) marl.

Conus odengensis K. Mart.   Plate III, fig. 2.

K. Martin, Foss. v. Java, 1, n. s., Pl. III, figs. 39–44.

The specimen figured here is a cast, and all casts are open to doubt, but it agrees with the form *C. odengensis* more nearly than with anything else it has been compared with.

Locality: Mount Mangilao, near Davao, Cebu, No. 272.

Formation: Miocene or Pliocene limestone.

Elevation: About 200 meters.

A form not greatly unlike this is *C. imperialis* Reeve living in waters near Bohol, specimen in Quadras collection, Bureau of Science, Manila.

Conus djarianensis K. Mart.   Plate III, fig. 3.

K. Martin, Foss. v. Java, Pl. III, figs. 45–50.

This seems to be identical with Martin's species.   It also resembles more or less closely *C. achetinus* Chem. and *C. arenatus* Brug., the latter living in the seas near Marinduque Island.

Locality: Raised beach, Bongao, Sulu Archipelago, No. 970.

Formation: Recent limestone.

Elevation: 5 meters.

Conus sp.   Plate III, fig. 4.

This is a small specimen which I did not compare directly with the Javan species, but with a figure merely.   I cannot be sure of the determination.   It is about the size and shape

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[20] These numbers refer to the localities where the fossils were collected; nearly all of these are shown on the locality map, Plate II.

of *C. parvulus,* but that species is lacking in the little tubercles on the spire which characterize this specimen.

Locality: Near Anda Island, Pangasinan, Luzon, No. 757.

Formation: Mio-Pliocene shale.

FUSIDÆ

FUSUS Lamarck

Fusus (Turbinella)

Shell spindle-shaped, mouth running forward in a canal, spire elongated, without cross furrows. Columella smooth with folds. Some 250 recent and at least 500 fossil species. Principal development in the Eocene and Miocene. The genus *Fusus* has been so split up by modern conchologists that Lamarck's name has quite disappeared from the literature. (*Zittel.*) Subgenera listed by Zittel, 15.

Species of Turbinella found fossil in the Philippines.

Fusus verbeeki K. Mart.
   Foss. v. Java, p. 85.
Turbinella ilocana sp. nov.
Fusus tjidamarensis K. Mart.
   Foss. v. Java, n. s., Pl. XIII, figs. 199 and 200.

Turbinella ilocana sp. nov. Plate III, fig. 8.
   Hörnes, Foss. Mollus. des Tertiär-Beckens von Wien, Pl. 31, fig. 2.

This corresponds very closely to *F. glomus* Gené, but is larger than the figured specimen of *glomus.* Some of the ribs in *T. ilocana* seem to be double and are closer together. Length, 51 millimeters; width of last whorl, 20 millimeters.

Locality: Cut in road between Pasuquin and Laoag. Ilocos Norte, Luzon, No. 356.

Formation: Recent marl.

Turbinella (Fusus) tjidamarensis K. Mart. Plate V, figs. 1, 2, and 3.
   Foss. v. Java, Pl. XIII, figs. 199 and 200.
   Fossils from the Cutch, India.

The Javan and Philippine specimens of this species differ apparently only in the shape of the mouth opening. In the Javan form the outer lip stands out like an ear, while in the Philippine form it is compressed and hugs the body whorl. In the Bureau of Science collection are 2 specimens from the same

locality which resemble very strongly *F. nodulosus* in the Indian Tertiary.

Locality: Slopes of Mount Mangilao, near Davao, Cebu.

Formation: Pliocene limestone, No. 272.

Elevation: 200 meters.

TRITONIDEA Swainson

Shell oval, inflected; spire and aperture of about equal length; surface usually spirally ribbed and transversely folded; columella often with weak transverse folds; outer margin thickened, crenate internally; aperture posterior with a short canal. Tertiary and Recent. (*Zittel.*)

Tritonidea (Pollia) ventriosa K. Mart.   Plate IV, fig. 16.

A specimen practically identical with this was figured and described by Martin as *Buccinum ventriosum*.[21]   Later he placed it in *Pollia*.   Dall has reverted to the earlier name for this genus.[22]

Locality: San Rafael, Agusan River Valley, Mindanao, No. 1054.

Formation: Recent shales.

BUCCINIDÆ

HINDSIA Adams

Shell ovately fusiform; spire acuminate; whorls longitudinally ribbed and cancellated; aperture ending anteriorly in a long recurved canal; inner lip thin, circumscribed, transversely corrugately plicated; outer lip grooved internally.   (*Zittel.*)

Hindsia dijki K. Mart.   Plate IV, fig. 17.

I have several specimens of *H. dijki* before me, which at first sight might be confused with *H. tambacana*.   They show slight variations from *H. dijki*, but in my opinion they are not specifically distinct.   These were compared directly with Martin's specimens.

Locality: Cut in road between Laoag and Bacarra, Ilocos Norte, Luzon, and the west side of Aroroy Bay, Masbate.

Formation: In (Ilocos Norte) recent sandy marl and (Masbate) in gray sandy shale, probably Pliocene.

[21] *Samml. d. geol. Reichs-mus. in Leiden*, 1, 204.
[22] I learned this in conversation with Doctor Dall.

VOLUTIDÆ

VOLUTA Linnæus

Last whorl very large; spire short with apex having warts or short spines; columella, frequently also the inner lip, possessed of several folds of which the anterior (lower) are strongest; canal very short, bent backward, frequently only a notch; with or without an operculum. (*Zittel.*)

Voluta sp. indet.   Plate XV, figs. 1, 2, and 3.

Casts like these are fairly common in certain limestone horizons, but it would be quite impossible to go beyond recognizing the genus in the case of these specimens at least. By far the greater part of the petrifactions found in the Philippines are in about this same imperfect state of preservation.

Locality: Batan Island, southeast coast of Luzon, No. 1.

Formation: Miocene limestone.

TURRICULA Adams

Shell fusiform to elongate, oval solid; transversely ribbed, spire high, acuminate; aperture narrow, channelled anteriorly; columella with numerous oblique folds, the posterior plaits being often the strongest; outer margin commonly thickened and smooth internally. Like *Mitra,* however, with cross ribs. The animals differ from each other in important characters of the radula. According to A. Adams there are 180 recent species. Fossils are abundant in the Tertiary. (*Zittel.*)

Turricula jonkeri K. Mart.   Plate IV, fig. 18.

K. Martin, Foss. v. Java, Pl. XI, figs. 175–177.

The Philippine specimen of *T. jonkeri* in our collection is smaller than the Javan specimens, and has one very distinct furrow near the top of each whorl. In the Javan form 3 ridges come somewhat closer together at this groove, but there is not the deep sharp suture which appears in the former. I do not believe this to be a specific difference, however.

Locality: Agusan River, Mindanao, No. 1054.

Formation: Recent or Pleistocene shales.

Turricula bataviana K. Mart.   Plate IV, fig. 19.

K. Martin, Foss. v. Java, Pl. XI, figs. 173 and 174.

Our specimens of this species are somewhat larger than the Javan ones with which I compared them. Also the edges of

all the transverse ribs in the former are smooth while in the latter they are slightly notched. This difference probably is due to wear.

Locality: San Rafael, Agusan River, Mindanao, No. 1054.
Formation: Recent or Pleistocene shales.

PLEUROTOMIDÆ

TURRIS Humph.

Spindle-shaped, long, the last whorl making up about one-half of the whole length of shell; canal elongated, generally straight; inner lip smooth. The sinus in the outer lip somewhat removed from the suture and located in a prominent roll. From the Cretaceous to present. (*Zittel.*)

Fossil species of Turris in the Philippines.

Pleurotoma gendinganensis K. Mart.   *Pleurotoma coronifera* K. Mart.
  Foss. v. Java, p. 32.   Foss. v. Java, p. 38.
Pleurotoma carinata Gray.   *Pleurotoma neglecta* K. Mart.
  Foss. v. Java, p. 37.   Foss. v. Java, p. 42.

Turris (Pleurotoma) andaënsis sp. nov.   Plate III, fig. 5.

A species which is superficially like the one figured here is *P. cataphracta* Brosc. (Foss. Wiener Beckens, Pl. 36, figs. 5 to 9.) However, on the prominent ridge or varix which follows the whorls there are 2 small tubercles instead of 1 on *cataphracta* and in general tubercles are more abundant on the former than on the latter. Height, 50 millimeters; width, 20 millimeters.

Locality; Anda Island, Pagasinan Province, Luzon, No. 757.
Formation: Miocene or Pliocene marl.

Turris (Pleurotoma) carinata Gray var. woodwardi.   Plate V, fig. 4.

  K. Martin, Foss. v. Java, Pl. VI, figs. 91–96.

This is almost identical with Javan specimens. As there is more or less difference between the young and the adult of some species, the minute difference in sharpness of ridges, height of whorls, etc. may be neglected.

Locality: Cut in road between Pasuquin and Laoag, Ilocos Norte, Luzon.
Formation: Recent sandy marl.

Turris (Pleurotoma) flavidula Lam. var. sonde K. Mart.   Plate III, fig. 7.

  K. Martin, Foss. v. Java, 1, n. s., Pl. VI, figs. 102–104.

A perfect specimen with beautiful proportions. Possibly slightly larger than the Javan forms. This was compared with Martin's figures, and not with the actual specimens as in most cases.

Locality: Bani, Pangasinan, Luzon, No. 758.

Formation: Pliocene (?) marl.

Elevation: 50 (?) meters.

Turris (?) agusana sp. nov.   Plate III, fig. 6.

This is a clean, white shell possessing almost its original polish, but with no trace of color. The aperture is not perfect so that it is difficult to place it exactly. I can find nothing quite like it either in the Quadras collection or in the literature. Although there is little trace of the byssal notch left, there is a shallow groove just below the suture which may represent it. The shell is 45 millimeters high and 17 millimeters wide, and its spire is sharply acuminate making an angle of 27°. Following the whorls are well-marked grooves about 1 millimeter apart, and between these are very fine cross striations. The sides of the whorls are flat.

Locality: Agusan River, Mindanao, No. 1054.

Formation: Recent or Pleistocene shale.

Elevation: About 50 meters.

NASSIDÆ

NASSA Martini

Shell ovate, inflated; aperture with short, reverted canal; inner lip callous, expanded, outer margin usually crenate internally.

Sparse in upper Cretaceous and Eocene; abundant in Miocene and Pliocene. Over 200 living species. (*Zittel.*) This is a worldwide genus in tropical seas.

Fossil species of Nassa in the Philippines.

Nassa verbeeki K. Mart.   *Nassa caniculata* Lam.
    Foss. v. Java, p. 110.   *Nassa siquijorensis* A. Adams.

Nassa caniculata Lamarck.   Plate IV, fig. 1.

    Reeve, Conch. Icon., 8, Pl. III, fig. 18.

This is quite the same as Cuming's specimens of a recent form from the Philippines with which I compared it directly. It also resembles *N. dertonensis* Bell.[23]

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[23] Sacco, Moll. Terz. del Piemonte, pt. XXX, Pl. XVI, fig. 61.

Locality: In bank, Agusan River at San Rafael, Mindanao, No. 1054.

Formation: Recent or Pleistocene shale.

Nassa verbeeki K. Mart.   Plate IV, figs. 2, 7, 8, and 10.

> K. Martin, Foss. v. Java, 1, n. s., Pl. XVII, figs. 247–255.

When I first compared the Philippine and Javan specimens I thought that the Philippine specimens represented a new species, but I found that in Martin's collection there was every variation existing among these specimens; namely, smoothness or roughness of the first whorl, slight upward projecting point of the lip, thickening just behind the edge of the aperture, and breadth of body whorl.

Locality: San Rafael, Agusan River, Mindanao, No. 1054.

Formation: Recent or Pleistocene shale.

Nassa siquijorensis A. Adams.   Plate IV, fig. 3.

> Reeve, Conch. Icon., 8, Pl. VIII, fig. 53.

The living form was collected by Cuming on the small Island of Siquijor, and the form shown here was compared directly with it in the British Museum.   With the exception of the somewhat more contracted aperture in the fossil specimen, there is no essential difference between the two.

Locality: San Rafael, Agusan River, Mindanao.

STROMBIDÆ

RIMELLA Agassiz

Shell spindel-shaped; surface cancellated; edge of the outer lip thickened, intact or notched; anterior canal short, the posterior channel more or less elongated, following the whorl. (*Zittel.*)

Rimella javana K. Mart.   Plate IV, fig. 4.

> K. Martin, Tertiärscht. auf Java (1880), Pl. IX, fig. 7.

The specimen shown on Plate IV was compared directly with the type in Leiden from which I could not distinguish it.

There is still another specimen in the Bureau of Science collection which, although somewhat mutilated, resembles *R. spinifera*.

Locality: San Rafael, Agusan River, Mindanao.

Formation: Pleistocene.

Elevation: About 50 meters.

<center>CASSIDÆ</center>

<center>**CASSIDARIA** Lamarck</center>

Shell ventricose, not varicose; canal long, twisted, reverted, or bent sidewise; inner lip greatly expanded; outer lip reflected, often crenulate; columella border plicate.   Upper Cretaceous to Recent, maximum in the Eocene.   (*Zittel.*)

Cassidaria echinophora Linn. (?)   Plate IV, fig. 5.

> Sacco, Moll. Terz. del Piemonte, pt. XXX, Pl. XXI, fig. 3.

I have compared this with a specimen from the Astian (middle Pliocene) of Italy, in the British Museum collection.   The living form in the same collection is different, the chief difference being in the matter of teeth on the inner side of the lip.   The prominent tooth near the upper portion of the lip in the Philippine form is lacking in the recent shell and the tubercles are more pronounced in the former.

Locality: Cut in road between Laoag and Bacarra, Ilocos Norte, Luzon.

Formation: Recent sandy marl.

<center>**CASSIS** Lamarck</center>

Shell ovoid, ventricose, having irregular varices; spire short, aperture elongate; outer lip thickened, reflected, usually denticulate in the interior; inner lip callous, expanded, denticulate, wrinkled, or granulate; canal very short, broad, sharply recurved, directed upward posteriorly.   Tertiary and Recent.   (*Zittel.*)

Cassis pila Reeve.   Plate V, fig. 6.

> Tryon, Conchology, 7, figs. 76, 77.

The form figured here and referred to *C. pila* is an imperfect cast, but sufficiently recognizable I think to be identified as this.

Locality: Constabulary Hill, in quarry at bottom of hill, Cotabato, Mindanao, No. 293.

Formation: Limestone.

Cassis nodulosa Gmelin.   Plate V, fig. 7.

This is a very recent form, and resembles closely a specimen in the British Museum collection marked "Her Majesty the Queen."

Locality: Bongao, Tawi Tawi, No. 970.

Formation: Recent, raised beach.

DOLIIDÆ

PYRULA Lamarck

This genus, established by Lamarck for pear-shaped shells with spires, is now broken up into a number of genera which are distributed among the families of Fusidæ, Purpuridæ, and Ficulidæ. In the paleontologic literature the collective name of *Pyrula* is generally retained. The genera belonging to the Fusidæ are: *Melongena, Fulgur,* and *Tudicla.*

Melongena Schumacher

Shell thick, pear shaped; spire short; whorls possessing tubercles or short spines; mouth long and oval; canal short and wide; columella smooth; outer lip plain. Tertiary and Recent. (*Zittel.*)

Pyrula (Melongena) sp.   Plate XIV.

This is a large imperfect cast which cannot be definitely placed.
Locality: Batan Island, southeastern coast of Luzon.
Formation: Miocene limestone.

DOLIUM Lamarck

Shell very thin, inflated; spire very short; body whorl very large, longitudinally and spirally ribbed or cancellated; aperture wide, oval; canal short, obliquely directed; outer lip notched internally. Cretaceous to Recent. (*Zittel.*)

Dolium costatum Menke.   Plate V, figs. 5 and 8.
    Tryon, Conchology, 7, Pl. IV, figs. 19–23.

Philippine specimens are very similar in every respect to those from Java, both groups of specimens being casts in a buff to yellow marl. One Philippine specimen is very much larger than the others and its ribs are farther apart, suggesting in general aspect *D. hochstetteri.*

In many cases the difference between *Dolium* and *Cassis* is not marked, and it also seems that they are closely related genetically.

The Javan specimens of *D. costatum* with nacreous outer layer in some cases show a single fine rib between the larger ones. This is true also in the case of some species of *Cassis.* This secondary rib is not always to be seen.

The matrix of both the Javan and Philippine specimens is very much the same, usually a buff to yellow marl.

Locality: Sibod Gulch, Naga, Cebu.
Formation: Miocene marl.

MELANIIDÆ

MELANIA Lamarck

Shell of various shapes, oval to turret shaped; smooth, spirally striated, ribbed or having nodes, at times with cross ribs or rolls; mouth always complete; columella gradually coalescing with the outer lip. Genus widespread over the earth with the exception of parts of North America. (*Zittel.*)

Melania laterita Lea. Plate IV, fig. 9.

     Reeve, Conch. Icon., 12, Pl. XXIII, fig. 164.

Locality: San Rafael, Agusan River, Mindanao.

Formation: Late Recent or Pleistocene shales.

Other specimens were collected in the Pasig River, Luzon, from mountain streams on Negros, and by Cuming. Another species occurring with this, but not figured here, is *M. denticulata.*

Melania woodwardi K. Mart. Plate VI, fig. 3.

     Martin, Foss. v. Java, 1, n. s., Pl. XXXVI, figs. 267–270.

This is figured here to show the general likeness between *Turritella,* a marine form, and a fresh-water form. The fresh-water shells are characteristically thinner shelled.

     Locality: Agusan River, Mindanao, No. 1054.

     Formation: Recent.

NATICIDÆ

NATICA Lamarck

Shell globose, semiglobose, or ovate; lustrous, rarely spirally striated, umbilicated or not; umbilicus when present, often partially or entirely filled with callous material; aperture semicircular or oval; outer lip sharp; inner lip thickened by a callus. Extremely abundant from the Trias on. (*Zittel.*)

Fossil species of Natica in the Philippine Islands.

Natica globosa Chem.
Natica marochiensis Gmel.
Natica rostalina Jenk. (?)

Natica globosa Chem. Plate IV, fig. 12.

     Reeve, Monogr. Ranella, Pl. II, fig. 46.

The specimens of this species in the Philippine collection resemble the Javan forms very closely, being, perhaps, a trifle more acuminate.

     Locality: Agusan River, Mindanao, No. 1054.

     Formation: Recent shales.

Natica marochiensis Gmel.   •

    Martin, Foss. v. Java, Pl. XXXVIII, figs. 616, and 617.

The Philippine form is larger, but in other respects, especially the umbilicus, it is an exact duplicate of the specimen from Java.

    Locality: Agusan River, Mindanao, No. 1054.

    Formation: Recent shales.

Natica rostalina Jenk. (?)

I found nothing in the Javan collection corresponding to this save one specimen labelled *N. rostalina.* The suture of the Philippine specimen is much deeper. The umbilicus is not visible.

    Locality: Cebu, white limestone cliffs, Minanga River on Toledo road, No. 277.

    Formation: Pliocene ?

Natica (Lunatia) sp.   Plate IV, fig. 13.

This may be merely a variety of *Natica globosa.* It is so small and featureless that it would not be safe to refer it definitely to any species.

Polynices (Natica) mamilla Lam.   Plate IV, fig. 14.

    Martin, Tertiärscht. auf Java (1880), 81.

The Philippine and Javan forms are so nearly identical that they might very readily be confused. In some of the older specimens from Java it was noted that the umbilicus had become completely filled with nacreous matter.

    Locality: Agusan River, Mindanao.

    Formation: Recent sandy shales.

TRITONIDÆ

BURSA Bolten

Shell oval or elongated, compressed front to back with 2 opposite lateral connecting varices; canal short, somewhat bent backward. Recent and Tertiary. (*Zittel.*)

Bursa (Ranella) subgranosa Beck.   Plate IV, fig. 15.

    Reeve, Monogr. Ranella, Pl. I, sec. 1.

The specimen in the Philippine collection differs only slightly from both the Javan forms of this species and *B. spinosa*, but is more like the former. A large number of specimens of these two species probably would show complete gradations

between the two.   In case of some of the smaller rows of nodes their larger or smaller size appears to be more or less fortuitous.
Locality: San Rafael, Agusan River, Mindanao, No. 1054.
Formation: Recent or Pleistocene shales.

Other Philippine species of Bursa.

Ranella spinosa Lam.	*Ranella raninoides* K. Mart.
Foss. v. Java, p. 131.	Samml. I, p. 203.
Ranella elegans Beck.	*Ranella gyrina* Linn.
Samml. III, p. 137 (Reichs-mus., Leiden).	*Ranella nobilis* Reeve.

Ranella spinosa and *Ranella nobilis* are in the Bureau of Science collection, occurring in Miocene or Pliocene shales at Aroroy, Masbate.   The others of the above list are in the Semper collection now in Leiden.

TURRITELLIDÆ

TURRITELLA Lamarck

Shell turret shaped; whorls even or arched, longitudinally ribbed or striated; aperture oval or rounded quadrilateral, rim not entire, external lip turned backward and somewhat bent outward.   Trias to Recent, maximum in the Tertiary.   (*Zittel.*)

Turritella terebra Lam.   Plate VI, fig. 1.

Lamarck, Mem. Soc. his. nat. Paris (1799), 74.

This species is still abundant in Philippine waters.   The specimen figured here is really a transition form between *T. bantanensis* with 3 pronounced ribs and *T. terebra* with 5 or 6. However, it more closely resembles *T. terebra*.
Locality: Excavations in Manila.
Formation: Alluvial sands, Recent.

Turritella cingulifera Sow.   Plate VI, fig. 2.

This is much larger than the Javan specimen with which I compared it, but it is clearly the same species.
Locality: Excavations in Manila.
Formation: Alluvial sands, Recent.

CERITHIIDÆ

VICARYA Jenkins

Shell turreted, whorls spirally marked; below the suture a row of protuberances; canal short and bent backward; inner lip flattened, callous; the outer lip beneath the row of spines

has a deep broad groove, which leaves behind a sutural band on the whorls.

Vicarya callosa Jenk. var. **semperi** Smith.   Plate VI, figs. 4, 6, 7, and 8.

> Quart. Journ. Geol. Soc. (1864), 20, Pl. VII, fig. 5; Tertiärscht. auf Java (1880), Pl. XI, fig. 3; Phil. Journ. Sci. (1906), 1, 628, Pl. III, fig. 1.

Fig. 4 is a drawing of a rather imperfect specimen, but which shows enough sculpturing to enable us easily to identify it. This specimen is from Batangas Province, Luzon, and is somewhat larger than those figured by Martin from Semper's collection (from Minanga and Dicamui Brook in northern Luzon), but is about the size of a specimen which I saw at the Imperial University of Tokyo. It is also about the same size as the one figured by Martin from Java.

This species is moderately common in the Philippine coal measure shales, being especially plentiful in the shale above the principal coal seam on the eastern end of Batan Island, Albay Province. It is also found in the same position in the coal measures in Cebu and Mindanao. It is a good "indicator" or zone fossil.

The characteristic features of all these specimens are the flattened whorls, the row of strong spines which is found next to the sutures, and the sigmoidal growth lines which have their deepest incurving between the rows of spines.

This is the most important and one of the most striking fossils to be found in the whole geological section in this part of the world.

It occurs in Japan, the Philippines, and Java, and there is a closely related form in India, *V. verneuili* D'Arch.

Locality: Loboo River, Batangas Province, Luzon; Cebu, Batan Island, and Mindanao.

Formation: Miocene (Gaj formation of India), shaly sandstone in Batangas, and in coal measure shale in the last-named localities.

CERITHIUM Adanson

Shell turreted, without epidermis; mouth oval, elongated anteriorly, with well-developed canal, with generally a short furrow posteriorly; operculum oval or semicircular with little

spiral coils. The oldest *Cerithium* occurs in the Alpine Trias. The principal development is in the Eocene. (*Zittel.*)

Cerithium (Campanile) sp.   Plate VI, fig. 5.

> Cf. P. Oppenheim, Die Eocänfauna des Monte Postale bei Bolea im Veronesichen, Paleontographica, **43**, Pl. XVI.

The fragment figured here is not exactly comparable to anything I have seen in any of the collections of Leiden or London, but is not greatly unlike some of the big campaniles of the Edward's Eocene collection in the British Museum. It is also like *C. vicentinum* Bay, or it might be compared with *Pyrazisinus haitiensis* Dall.

There is only one specimen in the Bureau of Science collection. There is a form, *Cerithium nodulosum,* living to-day in Philippine waters which is closely related to this fossil species, but in each of these species there is to be noted a little different alignment of tubercles or some other minor differences. If the specimen were more perfect I might venture to place it in some particular species, but for the present I shall be content with simply giving a figure of it.

Locality: Mount Mangilao, Danao, Cebu, No. 272.

Formation: Miocene limestone.

Potamides Brongniart

Shell turreted, with brown epidermis; mouth opening forward with weak canal or only a small conduit; operculum circular, multispiral. Brackish or fresh-water forms. (*Zittel.*)

Cerithium (Potamides) palustris Linn.   Plate VI, fig. 9.

> Martin, Foss. v. Java, Pl. XXXII, fig. 478.

This species inhabits only brackish water. The specimen figured here is smaller and more poorly preserved than the Javan specimens, but there can be little doubt that they are all the same species.

Other species in the Philippine collection are *P. noetlingi* K. Mart, *P. babylonicus* (?) K. Mart. and *P. herklotsi* K. Mart. *Potamides palustris* and *P. herklotsi* were found in coal measure shales with *Vicarya callosa* in the Tumaga River, near Zamboanga, Mindanao.

Formation: Miocene shale.

LAMELLIBRANCHIATA

SOLENIDÆ

AZOR Gray

Diagonally elongated; beak almost central; upper and lower margins straight and parallel; the two hinge teeth of the right valve very close, those of the left farther apart, the posterior tooth frequently stunted; the ligament nymphs wide, inflated; anterior muscle impression elongated, posterior pear shaped; surface marked by sharp lines. Cretaceous to Recent. (*Zittel.*)

Azor coarctatus Gm. Plate VII, fig. 1.

> *Tagelus* (*Solen*) *coarctatus* Gm.
> Linn. Syst. Nat. ed. 13 (1790), 1, 3227.

This form seems to be identical with *Tagelus coarctatus* collected by Cuming at Calaumana, Luzon. This species was first found near Naples and was figured in Reeve's monograph.

The shell is oblong, pale, fulvous, compound, covered with a wrinkled epidermis, narrowed in the middle, smooth, rather truncated, and open at each end; dorsal margin somewhat sloped. This is also very like *Psammosolen coarctatus* Gm. from the Vienna Basin.

Another specimen in the Bureau of Science collection, but not figured here, corresponds fairly well in external appearance to *Tagelus caribbæus* Lam.

Locality: San Rafael, Agusan River, Mindanao, No. 1054.

Formation: Recent shale.

Recently I found in the upper (Pliocene) limestone, Bondoc Peninsula, Tayabas Province, Luzon, a specimen—little more than an impression of one valve—of an *Azor*, about 25 centimeters long and 10 centimeters high. This is the largest specimen of this, living or fossil, I have ever seen.

CULTELLUS Schumacher

Shell narrow, strongly elongated, oval, compressed; lower margin curved, beak near the anterior margin; hinge teeth 1 : 2; anterior muscle impression round, posterior oval longitudinally; pallial ·sinus very wide, but short. Tertiary and Recent. (*Zittel.*)

Cultellus maximus Gm.   Plate VII, fig. 2.

This is a very fresh looking specimen which appears to have been covered with mud for only a very short time.   This species is still living.

Locality: San Rafael, Agusan River, Mindanao, No. 1054.

Formation: Recent or Pleistocene shale.

MYTILIDÆ

MODIOLUS Lamarck

Distinguished from *Mytilus* by the long trapezoidal or oval shape, by the slightly narrowed and rounded anterior portion, and by the weak beak lying somewhat behind the anterior edge. (*Zittel.*)

Modiolus sp.   Plate VII, fig. 3.

This specimen, except for a little distortion and one or two cracks, is excellently preserved.   Both valves are preserved, but slightly separated by the bluish white shale matrix.   The surfaces of the valves retain their original color and nacreous appearance.   I have no doubt but that this is a well-known form, but in the absence of adequate literature I shall refrain from attaching a specific name to it.   The specimen is about 6.5 centimeters long.   With the exception of the fine growth lines it has no sculpture.

Locality: Unknown (from the Spanish régime).

Formation: Shale, Recent?

CLEMENTIA Gray

Shell subtrigonal, transversely oval, inequilateral, white, slender, fragile; the hinge bearing 3 cardinal teeth upon each valve, the 2 anterior ones simple, vertical, and the posterior one bifid on the right side, the anterior is simple and the 2 posterior oblique on the left side; the ligament sunken; the interior edge of the valves simple, pallial sinus deep, ascendant.   (*Fischer.*)

Clementia sp.   Plate VII, fig. 4.

The specimen shown here, while fairly perfect, is only a cast so I am not able to make any specific determination.

Locality: Unknown, probably Cebu or Panay (from the Spanish régime).

Formation: Limestone.

Clementia papyracea Gray. Plate VII, fig. 5.

It is very difficult to tell whether this is a *Clementia* or a *Cytherea* from the cast. The Philippine forms resemble the above in many respects—shape, sculpture, etc.

Clementia is a recent genus according to Zittel, and, therefore, either it has a longer vertical range or these forms should not properly be referred to this genus.

Another internal cast is shown in Plate VIII, fig. 3.

Locality: About 0.5 kilometer west of the Tribunal, Baguio, Mountain Province, Luzon.

Formation: Tuffaceous sandstone.

Elevation: Nearly 1,500 meters.

VENERIDÆ

MACROCALLISTA Meek

(*Cytherea*)

External form and curve of the shell the same as in *Venus*, edges smooth; hinge with 3 dividing, frequently cleft teeth and in the left valve beneath the lunule a fourth, generally recumbent, anterior tooth, which corresponds to a long groove in the right valve; sometimes also there is a lateral tooth situated farther to the rear; pallial sinus large, triangular or tongue-shaped, sometimes quite lacking. This genus contains over 150 recent and at least as many fossil species which are widely distributed from the Jura to the older Tertiary. (*Zittel.*)

Macrocallista ventricola K. Mart. (?). Plate VII, fig. 6.

Martin, Tertiärscht. auf Java (1880), Pl. XVI, fig. 10.

This form resembles exteriorly *C. ventricola* described from the Tertiary of Java and it is also very similar to *Meretrix subpellucida* found in Luzon waters by Cuming.

Locality: Agusan River, Mindanao.

Formation: Recent deposits.

CHIONE Gray

(*Venus*)

Shell oval, roundish to triangular or heart-shaped, thick, smooth, or lined with ribs, striations, furrows, leaves, etc.; edges of shell finely crenulated, seldom smooth; a lunule usually is present; hinge area wide with 3 strong, diverging hinge teeth in each valve; ligament prominent; pallial sinus short angular. (*Zittel.*)

Chione (Venus) chlorotica Phil.   Plate VII, figs. 7 and 8.

Save for a slight difference in color which may be due to age or inclosing material these forms are identical with the Javan forms. Forms very closely allied to this, if not the same form, are living in Philippine waters to-day.

Locality: Agusan River, Mindanao, No. 1054.

Formation: Recent.

Chione (Venus) pulcherrima K. Mart.   Plate VIII, fig. 1.

Samml. d. geol. Reichs-mus. in Leiden (1891–1906), 1, n. s., Pl. XIII, fig. 47.

The form shown here may be a variety, for while the sculpture corresponds pretty well with the Javan form the latter is longer and not so high and perhaps slightly thinner. It also corresponds fairly well with *V. granosa* from the Cutch, India.

Locality: Opan, Mactan Island, about 3 meters above sea level, No. 275.

Formation: Pliocene or Pleistocene reef.

DOSINIA Scopoli

Shell circular, compressed, concentrically striated or grooved, with deep lunule under the beaks; hinge teeth 3, the right posterior and the anterior left are cleft; edges smooth, pallial sinus deep, ascendant pointed. About 100 recent species, fossils abundant in the Miocene and Pliocene. (*Zittel.*)

Dosinia boettgeri K. Mart.   Plate VIII, fig. 2.

Tertiärscht. auf Java (1880), Pl. XVI, fig. 4.

This is a rather young form, but not essentially different from the Javan species. These forms are casts and therefore allowance must be made for the difficulties in making exact determinations.

Locality: One-half kilometer west of the city hall, Baguio, Mountain Province, No. 41.

Formation: A very friable, reddish colored, tuffaceous sandstone; altitude, 1,500 meters.

PECTINIDÆ

PECTEN Klein

Shell round or higher than long, equivalved and apparently equilateral; free; upper surface mostly radially ribbed or striated; the anterior ears somewhat larger than the posterior, having on the right valve a deep byssal notch; hinge line straight,

the inner ligament in a central triangular hole just beneath the projecting beaks which touch one another; muscle impression large and subcentral.   (*Zittel.*)

Species of Pecten known from the Philippines.

Pecten fricatum Rv.	*Pecten sulcatus* Müll.
Pecten senatorius Gmel.	*Pecten subarcuatus* Bttg.
Pecten leopardus Rv.	*Pecten reticulatus* Rv.
Pecten solaris Rv.	*Pecten pallium* Linn.

None of these is mentioned in Martin's list in the appendix to Becker's report, and only one, *P. leopardus,* is given in Hidalgo's list of living species in the Philippines.

Pecten pallium Linn.   Plate IX, fig. 6.

    Martin, Tertiärscht. auf Java (1880), Pl. XX, fig. 10.

The form here shown is not exactly the same as *P. solaris* figured by Reeve.   The ears are partly worn off the Philippine form, and the secondary crenulations or small ribs are lacking in *solaris.*   In the Quadras collection of living shells I find a pecten with no specific name from Guam Island, one of the Marianne group.   This shell is about the same size as the fossil form shown here, and has practically the same crenulated ribs as well as the same number.   The living shell is strongly mottled red, brown, and white.

I have concluded, however, that this form is essentially the same as *P. pallium* described by K. Martin from the Tertiary of Java, though his specimen has one or two fewer ribs (a younger specimen, perhaps) and shows one ear missing.

    Plate X, fig. 1, shows a possible variety of the same species.

    Locality: Near Danao, Cebu, No. 272.

    Formation: Miocene limestone.

Pecten sulcatus Müll.   Plate IX, fig. 7.

    Müller, Zool. Dan. Prod. (1776), 248.

This form, although somewhat worn, is so closely like *P. sulcatus* that it is here referred to that species.   The fossil has the same number of ribs as the living form in the Quadras collection. There is a minor difference, however, namely the distance between the ribs.   This may be accounted for by wear.   The two forms are of about the same size.

    Locality: Talamban near Panoypoy, Cebu.

    Formation: Mio-Pliocene, upper coral limestone.

Pecten senatorius Gmel.

> Martin, Tertiärsch. auf Java (1880), Pl. XX, fig. 11.

At the time the plates for this paper were being drawn no good specimens of this form existed in the Bureau of Science collection, but since then several good specimens have been obtained from the "Upper Limestone" of Bondoc Peninsula, Tayabas, Luzon, which certainly belong to this species.

An imperfect specimen was also found in the Mio-Pliocene limestone near Danao, Cebu.

CHLAMYS Bolten

(*Æquipecten*)

Shell somewhat inequivalved, broadly rounded, anterior ears generally somewhat larger; outer surface radially striated or ribbed; ribs scaly or cross striated.   From the Trias to Recent. (*Zittel.*)

Chlamys (Æquipecten) (?) sp. indet.   Plate VIII, fig. 4.

> F. Sacco, Moll. Terz. del Piemonte, Pl. XXIV, fig. 1; and Pl. VII, fig. 11.

This is an incomplete specimen, the ears of which are entirely missing.   The nearest forms, which I have been able to find to which it bears any resemblance whatever, are *A. mioalternans* Sacco and *A. northamptoni* Micht. in the Pliocene of Italy.   I must say that I do not see much resemblance between this Philippine specimen and any species belonging to the genus *Chlamys*.

Locality: Liguan, Batan Island, southeast coast of Luzon, No. 1.

Formation: Upper limestone; Miocene or Pliocene.

SPONDYLIDÆ

SPONDYLUS Linnæus

Inequivalved, irregular, with the right valve attached, radially ribbed, spiny, or foliated; beaks unequal, in addition ears on each side; lower shell with a 3-cornered area in the middle of which for the most part is a row of pits.   The straight hinge line bears on each shell 2 very strongly curved teeth which fit into the corresponding holes of the opposite valve; between those there is a pit for the inner row.   The muscle impression is doubled, in old individuals, serrated.

The numerous recent species are best developed in the tropics and in the temperate zones, and are especially characterized by

their splendid ornamentation and striking colors.   The oldest fossil species are small, thin shelled, and have little ornamentation.   (*Zittel.*)

Spondylus sp.   Plate VIII, fig. 7.

The form here shown is only an internal cast, and therefore I am unable to place it specifically.   It is marked by 4 very strong and prominent ribs which extend downward into spines.
    Locality: Unknown.
    Formation: Limestone.

Spondylus ducalis Chem. (?)   Plate X, figs. 3 and 4.

    Mus. Bolten (2), 1798, 194.

This and the above are two specimens which belonged to the Spanish Mining Bureau, the labels of which were lost so that we know nothing definite about the locality or the horizon from which they came, except that they came from a limestone formation.

Spondylus ducalis is still living in Philippine waters on the coasts of Luzon, Cebu, and Mindanao.

The fossil shown here is flatter than *S. ducalis* and more worn. The flatness of the smaller valve may be due to compression or may be natural.

PLICATULA Lamarck

Shell irregular, flat or considerably arched with the beak of the right valve attached; smooth or wrinkled; hinge area indistinguishable, the ligament internal between two or more diverging ridge-like hinge teeth; the muscle simple and excentric. Numerous fossil species from the Trias on, as well as about 10 living.   (*Zittel.*)

Plicatula imbricata Menke.   Plate X, fig. 6.

    Sowerby, Plicatula 6 and 15–18.

Cuming collected this species on the beach of Corregidor Island at the entrance to Manila Bay.
    Locality: Sea cliff near Puerto Princesa, Palawan, No. 779.
    Formation: Recently elevated limestone.

LUCINIDÆ

LUCINA Bruguière

Shell more or less circular or lens shaped, compressed or bulging; the posterior side often has a furrow extending from the back to the posterior margin; lunule generally present; ligament exterior, frequently deeply sunken; hinge variable, generally

2 hinge teeth and 2 lateral teeth in each valve; frequently the lateral teeth are obliterated, sometimes also one or both of the hinge teeth; anterior muscle impression large, narrow, elongated toward the middle of the shell; posterior one oval, close to the margin; pallial line without indentation; inner surface inside the pallial line rough, frequently with a prominent furrow. One hundred living and at least 300 fossil species. (*Zittel.*)

Lucina (Codakia) sp.   Plate VIII, fig. 5.
    Cf. Proc. Malacolog. Soc., 3.

The species which I have been able to locate having the greatest resemblance to this form is *L. semperiana* Issel from the Andaman Islands. I do not see enough difference to lead me to place it elsewhere, nor do I feel sure enough of the diagnosis definitely to call it by this name.

Locality: Batan Island, southeastern Luzon, No. 4.
Formation: Miocene.

CARDIIDÆ

CARDIUM Linnæus

Shell inflated heart-shaped, sometimes narrow or longitudinally oval, closed or somewhat gaping; outer surface radially ribbed or striated, the ribs frequently possessing nodes or tubercles, edges crimped or toothed; hinge teeth 1, 2, 1:1, 2, 1; hinge and lateral teeth in their development somewhat weak. Two hundred recent species and from 300 to 400 fossil species. (*Zittel.*)

Cardium elongatum Brug.   Plate VIII, fig. 6.
    Ency. Mith. (Vers.) (1), 1789, 228.

The cast shown here is from the old Spanish Mining Bureau collection. Nothing is known either as to its locality or the formation it came from save that it must have been a limestone. It represents a young form probably.

This species is living in the waters near Panay and Jolo.

Cardium flavum Linn. (?)   Plate IX, fig. 1.
    Syst. Nat. ed. 10 (1758), 363; Reeve, Mon. fig. 68.

This form is another of a collection of relics from the Spanish régime, and nothing is known as to its locality. It is from a limestone formation. This species, if it is *flavum,* is still living in Philippine waters as indicated by Hidalgo.[24]

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[24] Catálogo de los Moluscos Testáceos de las Islas Filipinas. Madrid (1905), 344.

I judge from the nature of the petrefaction that it came from the Miocene-Pliocene limestone of Cebu or the same horizon on some other island, most probably Panay, as Abella did a great deal of his geological work on that island. This author mentions having found several species of *Cardium*.[25]

ARCIDÆ

ARCA Lamarck

Shell obliquely elongated, sides unequal, valves equal, more or less 4-sided, upper surface generally radially ribbed or striated, borders smooth or crenulated; beak forward of the center of the shell; through a more or less high, plane, rhombic area are "V"-shaped or bow-shaped furrows, separated from one another, for the insertion of the ligaments. The ligament covers the whole or a great part of the hinge area. Hinge line straight; teeth numerous, apparently of the same size, set diagonally to the hinge line and more or less parallel to each other. The numerous little cross teeth, perhaps, originate from two long drawn out ridge-like hinge teeth. The pallial line is simple, the two muscle impressions are comparatively large. (*Zittel.*)

Arca nodosa K. Mart. (?)   Plate IX, fig. 2.

Tertiärscht. auf Java (1880), Pl. XVIII, fig. 12.

The form shown here is closely related to *Arca nodosa*, although it does not show much development of nodes. It may be a variety or a young specimen.

A good specimen of this species was found recently on Bondoc Peninsula too late to be figured here.

Locality: San Rafael, Agusan River, Mindanao.

Formation: Recent shales in river bank.

Another species, which is given in Martin's list of the Semper collection, is *A. granosa* Linn. This has also been found recently in Bondoc Peninsula, Tayabas, Luzon.

The living fauna of the Philippines contains a great number of species of *Arca,* some of which are 5 or more centimeters in length.

PARALLELODONTIDÆ

CUCULLAEA Lamarck

Shell rhombic or trapezoidal, highly arched; beak separated by a wide hinge area; hinge line straight, in the middle little

[25] Descripción física, geológica y minera en bosquejo de la Isla de Panay. Manila (1890), 138.

cross teeth; laterally from 2 to 5 large ridge-like teeth parallel to the hinge line. The posterior muscle impression is frequently affixed to one or more strongly protruding thin plates. (*Zittel.*)

Cucullaea holoserica Rv. (?)   Plate IX, figs. 4 and 5.

The form here shown is another one of those left from the old Spanish collection and to which there is no label attached. It is also a cast, and therefore little that is definite can be said about it.

Locality: Either Cebu or Panay.

Formation: Limestone.

ASTARTIDÆ

CARDITA Bruguière

Shell oblate and 4-sided, very unequally sided, radially ribbed, edges toothed or crenulated; beak wide and thrust forward, ligament external; teeth 1 : 2 diverging and unequal. In addition there is a swelling-like process posteriorly developed. The muscle impression is strongly developed. From the Trias to the present. (*Zittel.*)

Cardita boettgeri K. Mart.   Plate IX, fig. 3.

Tertiärscht. auf Java (1880), Pl. XVII, fig. 10.

This specimen is somewhat worn so that the little nodes on the ribs do not show any longer. I compared it directly with the forms in Martin's Javan collection, and this Philippine form is a trifle smaller and has thicker ribs, but otherwise is quite the same.

Locality: Puerto Princesa, Palawan, No. 778.

Formation: Recent.

TRIDACNIDÆ

TRIDACNA Bruguière

Shell massive, 3-sided, with radial ribs, which have scaly leaves; margins deeply notched, the anterior side below the beak possessing a cleft for the byssus; hinge on either side with a recumbent hinge tooth and a moderately thick lateral tooth similarly situated. Recent and Miocene. Many species reach colossal size. (*Zittel.*)

The genus is common both fossil and living in the Philippines. One individual is reported to have measured 3 meters in length. I have seen one specimen 1 meter long.

Tridacna gigas Lam.   Plate XVI.   •
>   Mem. Soc. H. N. Paris (1799), 86.

This is only a fragment of an internal cast, but it is sufficient for determination.   The elevated reef limestones of the Philippines inclose many fragments and some fairly perfect specimens of this extraordinary shell.   The piece shown here represents a shell of about 25 centimeters' length, a young individual.

OSTREIDÆ

OSTREA Linnæus

Shell irregular, concentrically leaved or with large radial ribs and folds, arched, frequently compressed, margins simple, entire; hinge line toothless; beak frequently drawn out, straight with a hinge furrow across it on the underside.   Six subgenera including *Ostrea*.   *Alectryonia* in one of these.   Both valves with strong ribs, or folds, shell margins undulating or zigzag shaped. From the Trias on.   (*Zittel.*)

Ostrea sp.   Plate X, fig. 7.

This is a more or less characterless form which may be entirely normal or some freak form.   It may or may not be a new species.   If a new species were erected for every queer shape found in the genus *Ostrea,* the number would be legion.

>   Locality: Talamban near Panoypoy, Cebu, No. 274.
>   Formation: Mio-Pliocene limestone.

ALECTRYONIA Fischer

Shell distorted by early adherance to other objects, mononoyarian, the anterior adductor absent; edentulous, or with obscure schizodont dentition, dimyarian when young, the foot obsolete or absent in the adult; left valve attached to roots or branches by clasping shelly processes; both valves with strong, often divaricate folds and unduluate margins.   Trias to Recent. (*Zittel.*)

Alectryonia folium Linn.   Plate X, fig. 5.
>   Linnæus, Syst. Nat. ed. 10 (1758), 699.

Neither this genus nor species to my knowledge has been reported from the waters of the Philippines.   It does not appear in the Hidalgo catalogue.

>   Locality: Sea cliff near Puerto Princesa, Palawan, No. 779.
>   Formation: Recent.

THALLOPHYTA

CORALLINACEÆ

LITHOTHAMNIUM Philippi

The thallus of *Lithothamnium* grows attached to the face of a rock or other foundation, and forms a hard, stony mass, assuming various coralline shapes. The exposed face may have the form of numerous short branches, or an irregular warty surface. In section the lower part of the thallus is seen to be made up of rows of cells radiating from a central point, and the upper portion consists of vertical and horizontal rows of cells, the whole body is divided up into a large number of small cells by anticlinal and periclinal walls, and possesses an evident cellular, as distinct from a tubular, structure. Conceptacles containing reproductive organs are either sunk in the thallus or project above the surface. (*Seward.*)

Lithothamnium ramosissimum Reuss.   Plate XI, fig. 2.

> Nat. Abhandl. Haidinger (1848), 2, pt. 1, 29, Pl. III, figs. 10 and 11; Journ. Coll. Sci., Imp. Univ. Tokyo (1902), 17, art. 6, Pl. I, fig. 8.

The photomicrograph is from a thin section of the same limestone as that shown in fig. 1.

This form is widespread in the Miocene limestones in all parts of the Philippines as well as in adjacent islands outside the Archipelago. It is a typical "leit-fossil" or zone fossil characteristic of the middle limestone of the upper part of the Lower Miocene.

Locality: Lantauan Ridge, near Danao, Cebu, No. 286.

Formation: Limestone.

RHIZOPODA

RADIOLARIA

CENOSPHÆRA Ehrenburg

The test is a simple sphere without radial spines. The rounded outlines of forms of this genus are very common in all the radiolarian rocks of Borneo, but in most all traces of the structure of the test have disappeared. (*Hinde.*[26])

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[26] Reprint from Molengraaff's Borneo. Leiden (1899), 10.

Cenosphæra affinis Hinde.   Plate XX, figs. 1 and 2.

> Hinde, Descript. Foss. Radiolaria from rocks of central Borneo, appendix I in Molengraaff's Borneo (1899), Pl. I, fig. 7.

These 2 figures are photomicrographs of a section of an old slate from Bulacan Province found in 1912 by F. A. Dalburg. They show many individual Radiolaria, but only 2 or 3 specimens which can be plainly identified. The spherical form I have referred to *C. affinis*. The magnifications in the two figures are 100 and 200 diameters, respectively. In this specimen we find only the structure of the shell, the interior being completely taken up with a filling of cryptocrystalline silica.

DICTYOMITRA Zittel

The latticed test is conical or cylindrical without horn, and with an open basal aperture. The constrictions are horizontal. (*Hinde.*)

Dictyomitra tenuis Hinde.   Plate XX, figs. 1 and 2.

> Foss. Radiolaria from Central Borneo (1899), Pl. IV, fig. 15.

The oval-shaped section in these figures is thought to be a section of a form belonging to this species. These forms are all so generally devoid of any special character that there is reason for some latitude in their determination.

In Plate XII, fig. 1, is shown a section of a jasper from Ilocos Norte, Luzon, collected by me in 1906. I called attention to the resemblance of this specimen to the radiolarian cherts of California.[27] Since that time I have learned both from conversations with Dr. K. Martin in Leiden and from recent literature that similar jaspers and cherts have been found in Borneo, Java, and the Moluccas [28] and that they are there referred provisionally to the Jurassic.

In the Ilocos Norte jasper no distinct radiolarian characters could be made out, only small roundish areas filled with cryptocrystalline silica were visible.

Similar ancient-looking rocks have been found on Panay, on Balabac, and in Pangasinan Province, Luzon, but sections of the rocks collected by Dalburg in the Eastern Cordillera of Luzon were the first to show any determinable specimens.

[27] *This Journal, Sec. A* (1907), **2**, 158.
[28] Martin, Reisen in den Molukken. Leiden (1903), Geolog. Theil, Pl. VI, fig. 5.

FORAMINIFERA

NUMMULINIDÆ

OPERCULINA d'Orbigny

Shell typically complanate and planospiral with the whole of the convolutions visible; the earlier whorls more or less embracing; interseptal and marginal canals conspicuously developed. Lower Cretaceous to Recent. (*Chapman.*)

Operculina costata d'Orb.   Plate XIII, fig. 1.

Ann. sci. nat. (1826), 7, 281; Phil. Journ. Sci., Sec. D (1911), 6, 56.

This form is found in great numbers in the limestone cliffs along the Toledo road, Cebu, No. 277, about 3 kilometers west of Naga on the banks of the Minanga River. The formation is the upper limestone which dips gently to the southeast to the sea. Specimens in the Bureau of Science collection vary from 2 to 6 millimeters along the longest diameter.

ORBITOLITES Lamarck

Test discoidal, sometimes undulate or rarely sinous; growth either spiral (nonembracing) just at the commencement, or with one or more inflated, primordial chambers; subsequently cyclical; chambers more or less regularly divided into chamberlets. Upper Cretaceous to Recent. (*Chapman.*)

Orbitolites complanata Lam. (?)   Plate XIII, figs. 2, 3, and 4.

Phil. Trans. Roy. Soc. (1856), 224, Pls. V–IX.

The forms here shown apparently have the internal structure of this species, certainly in external appearance they are quite similar. They vary from 7 to 10 millimeters in diameter, and are less than a millimeter in thickness.

These were found by H. D. McCaskey some years ago on the beach of Semirara Island. He reported that they occurred there in great numbers, but was unable to say whether they had weathered out of a limestone or were recent forms. I am inclined to think they are very recent, although I am aware that the species goes back to the Cretaceous.

LEPIDOCYCLINA Gümbel

Median plane composed of chamberlets arranged in regular annuli around a distinct central chamber or chambers; thickened on either side by layers of flattened chamberlets more or less

irregularly disposed. The chief subgeneric types of *Orbitoides* are based on the appearance of the chamberlets of the median layer.

The genus *Lepidocyclina* has lozenge-shaped or spatulate-formed chamberlets. They occur in the Upper Cretaceous, the Oligocene, and the Miocene. (*Chapman.*)

Plate XI, fig. 1, is a photomicrograph of a thin section of the orbitoidal limestone on Lantauan Ridge about 12 kilometers west of Danao, Cebu. The horizon is probably uppermost Miocene.

Douvillé [29] has recognized the following species in sections of Philippine material which I submitted to him.

Lepidocyclina insulæ-natalis J. et Ch.   *Lepidocyclina smithi* Douvillé.
Lepidocyclina richthofeni Smith.   *Lepidocyclina verbeeki* Newt. et Holl.
Lepidocyclina formosa Schlumb.   *Lepidocyclina inflata* Provale.
Lepidocyclina inermis Douvillé.   *Lepidocyclina* cf. *marginata* Mich.

I shall figure only two species here.

Lepidocyclina insulæ-natalis Jones et Chap. Plate XIII, figs. 6 and 7.

> Monograph Christmas Island. London (1900), Pl. XX, fig. 5.
> Samml. d. geol. Reichs-mus. in Leiden (1888–1902), I, 6, 128.

These are very much enlarged drawings of the swollen central portion of this species. These pea-like swellings from which the surrounding wing-like parts have been worn away are more common than the whole specimens.

Figs. 13, 14, 15, and 16 are drawings of various fragments of the same. These were all found lying loose on the surface of the small hill in the lower Kahumayhumayan Valley in Cebu. The original containing-limestone has been removed, and the underlying rock was found to be coal measure shale. I feel convinced that these forms were weathered out of a limestone which lay stratigraphically below that on the neighboring hill summits.

Similar forms have been found in Java and Christmas Island, and doubtless they are pretty generally distributed in this region. Those from Christmas Island have been determined by Chapman as *L. insulæ-natalis,* though Douvillé figures practically the same thing as *L. richthofeni* Sm. This last name, however, was given by me, at an earlier date, to an entirely different form of which the chief outward character was its more bulging and rounded shape.

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[29] *This Journal, Sec. D* (1911), 6, 71–74.

Lepidocyclina formosa Schlumb. (?)   Plate XIII, figs. 8, 9, 11, and 12.

> Samml. d. geol. Reichs-mus. in Leiden (1900), I, 6, Pl. VII, figs. 1–3, 251; Phil. Journ. Sci., Sec. D (1911), 6, 72, Pl. D. figs. 2–5.

Similar forms have been described and figured by Douvillé. Plate XIII, fig. 5, shows a fragment of orbitoidal and coralline limestone from Guila-Guila in Cebu, illustrating the characteristic appearance of this rock and the abundance of the remains therein.

COELENTERATA

LITHOPHYLLIACEÆ

MONTLIVAULTIA Lamouroux

Free, pedunculate, or attached by a wide base, cylindrical, circular, or oval shaped; epitheca thick, but fragile and often rubbed away; septa numerous, wide, regularly toothed; columella lacking; cross plates strong and numerous. Common in the Jura, not so well developed in the Trias, Cretaceous, and Tertiary. (*Zittel.*)

Montlivaultia bulacana sp. nov.   Plate XVII, figs. 1 and 3.

These two specimens though differing considerably in size and shape are referred to the same species as it is thought that the specimen shown in fig. 3 is somewhat distorted. The specimens are 6 and 10 centimeters long and 3.5 and 4.5 centimeters wide, respectively. They were pedunculate. The septæ are on the average 1 millimeter apart, and are apparently parallel from the base to the edge of the calyx. At intervals, which are not constant, there are lines perpendicular to the septæ running around the calyx which may denote horizontal tabulæ. These forms roughly simulate *Streptolasma* from the Silurian, but in the latter the septæ diverge fan-like from a median line.

Locality: San Miguel de Mayumo, Bulacan, Luzon, No. 189.

Formation: Limestone.

One of these forms is not greatly unlike *Turbinolia hippuritiformis* Michelin,[30] which occurs in the cretaceous of France.

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[30] Zoöphyta Iconica. Paris, 287, Pls. 65–67. Compare, also, The fossil corals and Alcyonaria of Sind, *Mem. Geol. Surv. India*, 2, Pl. V, fig. 9.

Montlivaultia robusta sp. nov.   Plate XVII, fig. 6.

This specimen differs from the other two in being more robust and having a larger base.

Locality: San Miguel de Mayumo, Bulacan, Luzon.

Formation: Limestone.

All of these specimens are in outward appearance somewhat like montlivaultias from the nummulitic of India, Lukkee, southern Indus Range, and now in the British Museum.

Montlivaultia cortada sp. nov.   Plate XVIII, fig. 1.

This species is very different from those already shown.   It is quite stumpy in appearance, but has all the generic characters of *Montlivaultia*.   It is pedunculate like the others shown.   It is a trifle wider at the top than it is long, the length being 2 centimeters.   The base is small, and the sides make an angle of about 75°.

Locality: Beach at Caracaran, Batan Island, southeastern Luzon, No. 2.

Formation: Shale, probably Miocene.

PATTALOPHYLLIA d'Ach.

Circular, short attachment, somewhat compressed laterally; calyx elliptical; wall naked, covered with fine ribs; septa numerous, serrate; columella lamellar-like or rudimentary, surrounded by a manifold circle of long, ragged rods.   Eocene. (*Zittel.*)

Pattalophyllia (?) bonita sp. nov.   Plate XVIII, figs. 4 and 5.

E. Osassco, Paleontographica italica, 8, 99, Pl. I, figs. 3 and 3b.   Mem. Geol. Surv. India, ser. XIV, I, 2, Pl. XX, figs. 1–3.

Calix almost circular in plan, inverted shallow cone.   Deep sinus where columella should be.   Height, 1 centimeter; diameter of crown of calyx, 2.5 centimeters.

This specimen resembles a form under the name *Calyptraea rugosa* Noetling from the Miocene of Burma.   The name *Calyptraea,* however, according to Zittel has already been used for one of the Platypoda.

It is also very similar to *Trochocyathus nummiformis* Duncan from the Tertiary deposits of the Sind, India.   The Philippine form is deeper and has an elliptical hollow in the center, features which readily distinguish it from the Indian species.

The closest resemblance, however, is to the figures in Osassco's

work, so that the Philippine form might also be referred to *P. cyclolitoides.*

Locality: Barrio Mesaba, near Danao, Cebu, No. 272.

Formation: Miocene limestone.

CARYOPHYLLIA Stokes

Circular, with attached, spread out base; calix circular; columella bundle shaped, consisting of little twisted rods; septa wide and projecting; ribs simple; pale, wide, throughout most of their length; free, Cretaceous, Tertiary, living.   (*Zittel.*)

Caryophyllia (?) laoagana sp. nov.   Plate XVIII, figs. 2 and 3.

> Foss. Corals and Alcyonaria of Sind, Pl. I, figs. 2 and 3.   Pal. Indica, 1.

The specimen here shown more nearly resembles *C. compressa* Duncan than anything I have been able to find in the literature. It differs a good deal in shape, but this may be due to distortion or partial mutilation of the specimen.

The columella is not visible in the Philippine form so that I cannot refer it to the genus *Caryophyllia* with certainty.   It seems to be decidedly more curved than the Indian form, and on the basis of these differences I am giving it a specific name. Length, 17 millimeters; width at widest part of the calyx, 14 millimeters.

Locality: Cut in road near Laoag, Ilocos Norte, Luzon, No. 356.

Formation: Pleistocene or Recent marl.

TURBINOLIDÆ

FLABELLUM Lesson

Sraight; compressed; free or fixed; columella rudimentary; septa numerous, not projecting; wall with epitheca and covered with spines and ridges.   Tertiary to Recent.   (*Zittel.*)

Flabellum australe Moseley (?)   Plate XVIII, fig. 7.

> Challenger Reports, Zool. (1881), 2, 173, Pl. VII, figs. 4, 5.

The forms here shown resemble fairly closely in general appearance those figured in the Challenger Reports.   However, there are differences to be noted.   The Philippine form shows a smaller number of septa, and the 2 sharp end edges make a wider angle with the base than in *F. australe.*   These differences in my opinion are not enough to warrant calling this more than a variety of *F. australe.*

There are some specimens in the Bureau of Science collection so broken that the columella, which is not visible in the entire specimens, is visible nearer the base.

Locality: West side of Aroroy Bay near Point Colorado, Masbate, No. 588.

Formation: Mio-Pliocene shale.

This species has been found living at depths varying from shallow water to 1,500 fathoms.

The specimen shown on Plate XII, fig. 10, is also a *Flabellum*, but it is too small and imperfect a specimen to be specifically determined.

ODONTOCYATHUS Moseley

Corallum with a fasicular columella and 3 crowns of pali, free but with a minute scar of former attachment, in the form of a deep saucer, with straight sloping sides and a broad flat base composed of fused radiating tuberculate spines which project like the spokes of a wheel all round the base of the wall. (*Moseley.*)

Odontocyathus coloradus sp. nov.   Plate XVIII, fig. 8.

This species is essentially the same as *O. coronatus* Moseley save for one striking difference, the possession of 6, instead of 12, spines projecting from the base.   This may be fortuitous, but I am inclined to think not.   The exterior wall is smooth and more rounded in the Philippine form.   Diameter of calix, 25 millimeters; height, 15 millimeters.

Locality: Point Colorado, Aroroy Bay, Masbate, No. 588.

Formation: Miocene or Pliocene shale.

LOPHOSERINÆ

CYCLOSERIS Edwards et Haime

Free, disk shaped, circular; wall horizontal, naked with fine granulated ribs, septa numerous, finely toothed on the upper edge, the smaller ones intergrown on the inner edges with the larger. Cretaceous, Tertiary, and Recent.

Cycloseris decipiens K. Mart.   Plate XVII, fig. 5.

Tertiärscht. auf Java (1880), 146, Pl. XXV, fig. 3–6.

The specimen shown here is more perfect than the one figured by Martin and has a hole in the center, which is entirely filled up in the Javan form, otherwise the two are very nearly identical.

I frequently have found this form on dead reefs along the coasts, and it is my impression that the species is still liv-

ing, although it may have another name.   Closely allied, but
smaller, forms have been found at over 1,500 meters' elevation at
Baguio, Luzon.

Locality: Ilaga River, Batangas, No. 24.

Formation: Miocene or Pliocene limestone.

PACHYSERIS Edwards et Haime

(*Undaria*)

Stock attached, leafy; calices arranged in simple rows sepa-
rated by comb-like ridges, the rows completely coalescing; septa
fine, crowded together; columella warty, well developed.   Eocene,
Oligocene, and Recent.   (*Zittel.*)

Pachyseris cristata K. Mart. (?)   Plate XVIII, fig. 9.

Tertiärscht. auf Java (1880), 145, Pl. XXVI, fig. 8.

This is more like *P. cristata* than any other of the Javan species
with which I have compared it.   The Philippine specimens show
much more irregularity in the ridges, and the septa appear to be
somewhat finer.

Locality: Barrio Mesaba, Danao, Cebu, No. 272.

Formation: Miocene limestone.

PTYCHOCYATHUS (?)

Ptychocyathus (?) incognitus sp. nov.   Plate XVIII, fig. 10.

In this specimen, the stock consists of two long calices joined
by the coalescing of the epitheca of the walls.   The calices are
circular in section.   At the top they measure in diameter about
2 centimeters, and they taper almost to a point.   The walls are
about 3 millimeters in thickness, and strongly corrugated with
deep V-shaped grooves which run the length of the corallite.
Length of the specimen 7 centimeters.   Nothing of the internal
structure can be made out as it is filled with recrystallized
calcium carbonate.

Locality: Unknown.   Spanish collection.

Formation: Limestone.

SPONGIÆ

LITHISTIDÆ

CHENENDOPORA Lamouroux

Beaker, funnel or cup shaped, thick walled, generally with
stem; inner side with small sunken osculis from which simple,
generally bent, canals penetrate deeply the thick wall.   The
canals take a more downward inclination, and extend as vertical

tubes in the stem. The surface is covered with fine pores or krinkled integument. Skeleton consists of gnarled, branching, warty protuberances possessing little lithistid bodies. (*Zittel.*)

Chenendopora (?) major sp. nov.   Plate XVII, fig. 2.

> Michelin, Iconographie Zoöphytologique, 324, Pl. 77, fig. 13a.

I am unable, owing to the state of the petrifaction of this specimen, to say definitely in what genus it should be placed.   It is unlike any thing in either the British Museum or the Leiden collections.   It may be a *Cellepora* as it is superficially not unlike illustrations of *Cellepora cucullina* Mich.   The surface under a hand lens is seen to be perforated by innumerable minute pores. The figure is reduced to one-fourth actual size.

Locality: Liguan, Batan Island, southeastern Luzon, No. 1.

Formation: Miocene limestone.

MADREPORIDÆ

MADREPORA Linnæus

Stock branching, bundle shaped, or lobulated, consisting of small cells lying in a spongy net-like cœnenchym; calix prominent (especially in the young) with thick edge; septa not projecting; visceral cavity divided into halves by 2 septa, opposite and touching one another on the inner edges; columella lacking.   Tertiary and Recent.   (*Zittel.*)

This is the principal reef-building coral of the present time, but is not common in the Tertiary except in the tropics.

Madrepora duncani Reuss. (?)   Plate XVIII, fig. 6.

> Tertiärscht. auf Java (1880), Plate XXV, fig. 11.

The polyp cavities are larger in this specimen than in Martin's Javan form and are slightly farther apart.   These differences do not seem to be of specific value, and the state of the specimens does not justify any discrimination.

Locality: Barrio Mesaba, near Danao, Cebu, No. 272.

Formation: Miocene limestone.

ASTREACEÆ

PRIONASTRAEA Edwards et Haime

Stock convex or uneven, walls commonly with thin epitheca; bud submarginal, besides calycinal union; cells closely crowded, prismatic, walls united interiorly above, separated below; calyx polygonal, deep, with simple borders; columella spongy; septa thin, close, granulated, and serrate, the largest teeth in the neighborhood of the centrum.   Tertiary and Recent.   (*Zittel.*)

Prionastraea (?) vasta Klz.   Plate XVII, fig. 4.

   Die Korallthiere des Rothen Meeres—Klunziger, Pl. IV, fig. 8.

This is not an especially good specimen on which to base any comparisons, but most of our fossil corals are in no better condition.   I have referred this to the above species for the reason that it looks more like the illustrations of this species than any others which I had access to.   I am inclined to question the genus because of the arrangement of the septa, which should be thin and closer together than are those in this specimen.

Locality: Caracaran River, Batan Island, southeastern Luzon, No. 2.

Formation: Limestone.

HYDROID ZOÖPHYTES (?) Plate XIX, fig. 6.

It is not clear just what these specimens are.   An examination by a specialist is needed definitely to identify these low forms which are on the borderland between plants and animals.   They are abundant in the uppermost limestones of parts of Mountain Province of Luzon.

Locality: On the ridge west of Mount Mirador, Baguio, Mountain Province, Luzon, No. 45.

Formation: Pliocene (?) limestone.

ECHINODERMATA

ECHINOIDEA

SPATANGIDÆ

SCHIZASTER Agassiz

Periproct excentric, posterior; ambulacra in unequal pairs, the anterior pair strong and directed forward, somewhat bent and nearer the groove of the unpaired ambulacrum, the latter deep and grooved along the edges; the double pores of the anterior ambulacrum crowded and numerous.   Principal development in the Tertiary, seldom living.   (*Zittel.*)

Schizaster subrhomboidalis Herkl.   Plate XIX, fig. 1.

   Tertiärscht. auf Java (1880), Anhang 5.

The specimen figured here, although not a perfect one, due to some distortion and a hard encrusting matrix, answers in general the description of this species, although I have not compared it with any specimen or drawing.   After the drawings for this plate were completed several very perfect specimens of this species were collected from the Miocene of Bondoc Peninsula,

Tayabas Province, Luzon. These are all quite like those described by Martin from Java.

Locality: White cliffs on Minanga River, Cebu, No. 277.

Formation: Mio-Pliocene limestone.

SCAPHOPODA

SOLENOCONCHÆ

DENTALIUM Linnæus

Shell tube shaped, elongated, conical, symmetrical, somewhat bowed, gradually tapering toward the posterior end; open at both ends; exterior surface longitudinally striated, ribbed, or smooth; anterior opening simple not constricted, posterior small. Numerous, mostly large, species occur in the Miocene and Pliocene. (*Zittel.*)

Dentalium tumidum sp. nov. Plate XIX, fig. 2.

The fragment figured here is only about 2 centimeters long, but it is believed that it is sufficient to show the characters of the species. The unusual cross-section showing the lateral bulging and thickening of the walls is apparently quite unique. I have been unable to locate any specimen or illustration of any form just like it, so I have given it the specific name *tumidum* to note this prominent character.

This specimen is longitudinally striated like many other species of *Dentalium.* At the widest part the diameter is 12 millimeters; along the shorter diameter, 9 millimeters. The shell tapers gradually as in other species of the genus.

Locality: Agusan River, Mindanao, No. 1054.

Formation: Pleistocene or Recent shales.

PLATYPODA

VERMETIDÆ

VERMETUS Adanson

Shell usually attached, irregularly tubular, internally vitreous, and often with septa. Carboniferous (?) to Recent. Abundant in the Tertiary. (*Zittel.*)

Vermetus giganteus K. Mart. Plate XIX, fig. 5.

Tertiärscht. auf Java (1880), 78, Pl. XIV, fig. 15.

An almost identical form from Java is figured by Martin under the name of *Septarea arenaria* Linn., but in the text he calls it *V. giganteus* n. sp.

These tubular forms are so characterless, especially in the fossil state, that it is particularly difficult to establish new species among them.

Locality: Barrio of Mesaba, near Danao, Cebu.

Formation: Miocene limestone.

ARTHROPODA

THALASSINIDÆ

CALLIANASSA Leach

Body with the exception of the claws soft skinned; cephalothorax small, compressed, abdomen very long and narrow, first segment thin and short; caudal fin large; the claws of the first pair of legs large and unequal, laterally much flattened, the sharp edges set with fine serrations; movable finger joined to the propodite and surrounded on both sides by a collar-shaped process ("ball and socket" joint); carpodite straight, united with the propodite, of like shape and width as this, but shorter and rounded and tapered posteriorly; the rest of the parts of the claws markedly narrower and smaller. By the equal development of the carpo- and propodite the claws of *Callianassa* are distinguished from those of other crustacea. Recent and fossil from the Jura on. (*Zittel.*)

Callianassa dijki K. Mart. Plate XIX, figs. 3 and 4.

These were compared directly with specimens in the Leiden collection of Javan fossils and found to be quite the same. The two parts shown here are propodites; that is, the joints of the claw next to the movable finger or pincer.

I have never found any other parts of this animal save the two last joints of the claw. They are quite common in Cebu in the shale just above the large Compostela coal seam.

Locality: Old Compostela coal mines, Mount Licos, Cebu, No. 289.

Formation: Miocene shale.

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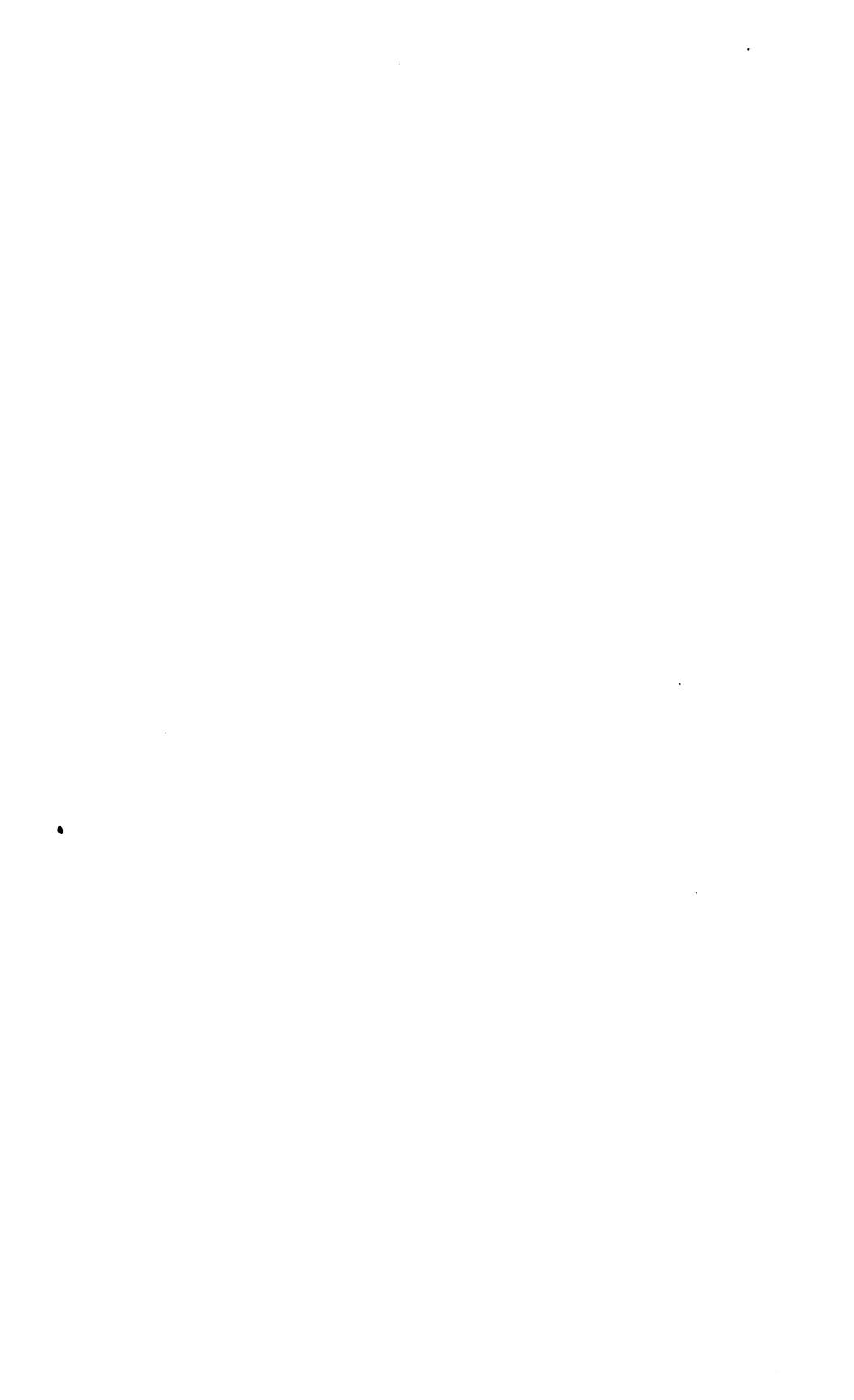
ILLUSTRATIONS

Plates 3, 7, 8, 18, and 19 are from drawings by P. Moskaira and G. Gomez; Plates 4, 5, 6, 9, and 10 are from drawings by G. Gomez; Plate 13 is from drawings by P. Moskaira; Plates 11, 12, and 20 are from photomicrographs by Charles Martin; Plates 14 to 17 are from photographs by E. Cortes.

PLATE I

Generalized geological map of the Philippine Islands.

PLATE II

Map of the Philippine Islands showing fossil localities.

PLATE III

Fig. 1. *Conus sulcatus* Brug. var. *philippinensis* var. nov.
2. *Conus odengensis* K. Mart.
3. *Conus djarianensis* K. Mart.
4. *Conus* sp.
5. *Turris (Pleurotoma) andaënsis* sp. nov.
6. *Turris (?) agusana* sp. nov.
7. *Turris (Pleurotoma) flavidula* Lam. var. *sonde* K. Mart.
8. *Turbinella ilocana* sp. nov.

PLATE IV

Fig. 1. *Nassa caniculata* Lamarck.
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3. *Nassa siquijorensis* A. Adams.
4. *Rimella javana* K. Mart.
5. *Cassidaria echinophora* Linn. (?)
6. *Nassa caniculata* Lamarck.
7. *Nassa verbeeki* K. Mart.
8. *Nassa verbeeki* K. Mart.
9. *Melania laterita* Lea.
10. *Nassa verbeeki* K. Mart.
11. *Nassa* sp. indet.
12. *Natica globosa* Chem.
13. *Natica (Lunatia)* sp.
14. *Polynices (Natica) mamilla* Lamarck.
15. *Bursa (Ranella) subgranosa* Beck.
16. *Tritonidea (Pollia) ventriosa* K. Mart.
17. *Hindsia dijki* K. Mart.
18. *Turricula jonkeri* K. Mart.
19. *Turricula bataviana* K. Mart.

PLATE V

FIGS. 1 to 3. *Turbinella tjidamarensis* K. Mart.
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    5. *Dolium costatum* Menke.
    6. *Cassis pila* Reeve.
    7. *Cassis nodulosa* Gmel.
    8. *Dolium costatum* Menke.

PLATE VI

FIG. 1. *Turritella terebra* Lam.
    2. *Turritella cingulifera* Sow.
    3. *Melania woodwardi* K. Mart.
    4. *Vicarya callosa* Jenk. var. *semperi* Smith.
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FIG. 1. *Azor coarctatus* Gmel.
    2. *Cultellus maximus* Gmel.
    3. *Modiolus* sp.
    4. *Clementia* sp.
    5. *Clementia papyracea* Gray.
    6. *Macrocallista ventricola* K. Mart. (?)
    7. *Chione (Venus) chlorotica* Phil.
    8. *Chione (Venus) chlorotica* Phil., interior.

PLATE VIII

FIG. 1. *Chione (Venus) pulcherrima* K. Mart.
    2. *Dosinia boettgeri* K. Mart.
    3. *Clementia* (?), internal cast.
    4. *Chlamys (Æquipecten)* (?) sp. indet.
    5. *Lucina (Codakia)* sp.
    6. *Cardium elongatum* Brug.
    7. *Spondylus* sp., internal cast.

PLATE IX

FIG. 1. *Cardium flavum* Linn. (?)
    2. *Arca nodosa* K. Mart. (?)
    3. *Cardita boettgeri* K. Mart.
    4. *Cucullaea holoserica* Reeve (?), cast.
    5. Same as fig. 4, end view.
    6. *Pecten pallium* Linn.
    7. *Pecten sulcatus* Müll.

PLATE X

FIG. 1. *Pecten (Chlamys)* sp.
2. A coralline form, undetermined.
3. *Spondylus ducalis* Chem. (?)
4. *Spondylus ducalis* Chem. (?), lower value.
5. *Alectryonia folium* Linn.
6. *Plicatula imbricata* Menke.
7. *Ostrea* sp.

PLATE XI

FIG. 1. Orbitoidal limestone, Cebu.
2. *Lithothamnium ramosissimum* Reuss.

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FIG. 1. Section of radiolarian chert from near Nagpartian, Ilocos Norte, Luzon.
2. Foraminiferal limestone, Batan Island.

PLATE XIII

FIG. 1. *Operculina costata* d'Orbigny.
2. *Orbitolites complanata* Lam.
FIGS. 3 and 4. *Orbitolites*, sections, much enlarged.
FIG. 5. Orbitoidal and coralline limestone.
FIGS. 6 and 7. *Lepidocyclina insulæ-natalis* Jones et Chap., central part.
FIG. 8. *Lepidocyclina formosa* Schlm. (?)
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Pyrula (Melongena) sp. indet.

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PLATE XVII

FIG. 1. *Montlivaultia bulacana* sp. nov.
2. *Chenendopora (?) major* sp. nov.
3. *Montlivaultia bulacana* sp. nov.
4. *Prionastraea (?) vasta* Klz.
5. *Cycloseris decipiens* K. Mart.
6. *Montlivaultia robusta* sp. nov.

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FIG. 1. *Montlivaultia cortada* sp. nov.
FIGS. 2 and 3. *Caryophyllia (?) laoagana* sp. nov.
      4 and 5. *Pattalophyllia (?) bonita* sp. nov.
FIG. 6. *Madrepora duncani* Reuss (?)
      7. *Flabellum australe* Moseley (?)
      8. *Odontocyathus coloradus* sp. nov.
      9. *Pachyseris cristata* K. Mart. (?)
      10. *Ptychocyathus (?) incognitus* sp. nov.

PLATE XIX

FIG. 1. *Schizaster subrhomboidalis* Herkl.
      2. *Dentalium tumidum* sp. nov.
FIGS. 3 and 4. *Callianassa dijki* K. Mart.
FIG. 5. *Vermetus giganteus* K. Mart.
      6. Hydroid zoöphytes (?) in limestone block.

PLATE XX

FIG. 1. Section of old "slate" (?) containing Radiolaria.   ×100.
      2. The same specimen as that in fig. 1.   ×200.

GENERALIZED GEOLOGICAL MAP
OF THE
PHILIPPINE ISLANDS

Made under the Direction of
Warren D. Smith

from surveys by members of the
Division of Mines, Bureau of Science.
Manila P. I.
1913

PLATE I. GENERALIZED GEOLOGICAL MAP OF THE PHILIPPINE ISLANDS.

Plutonic and older extrusives.

Metamorphic.

Pre-Tertiary sediments and doubtful rocks.

Tertiary sediments.

Recent volcanics.

Tuff.

Alluvial and littoral.
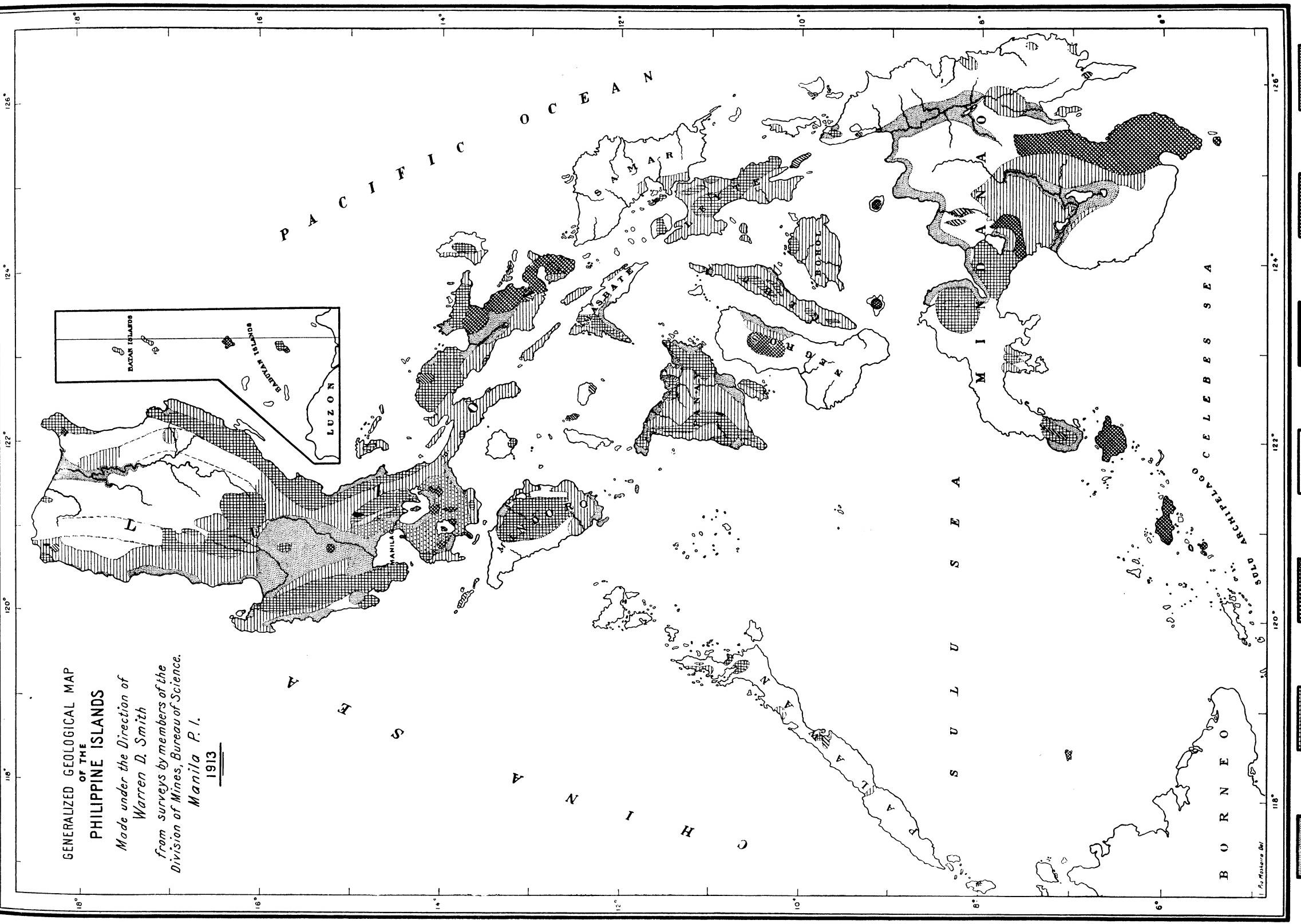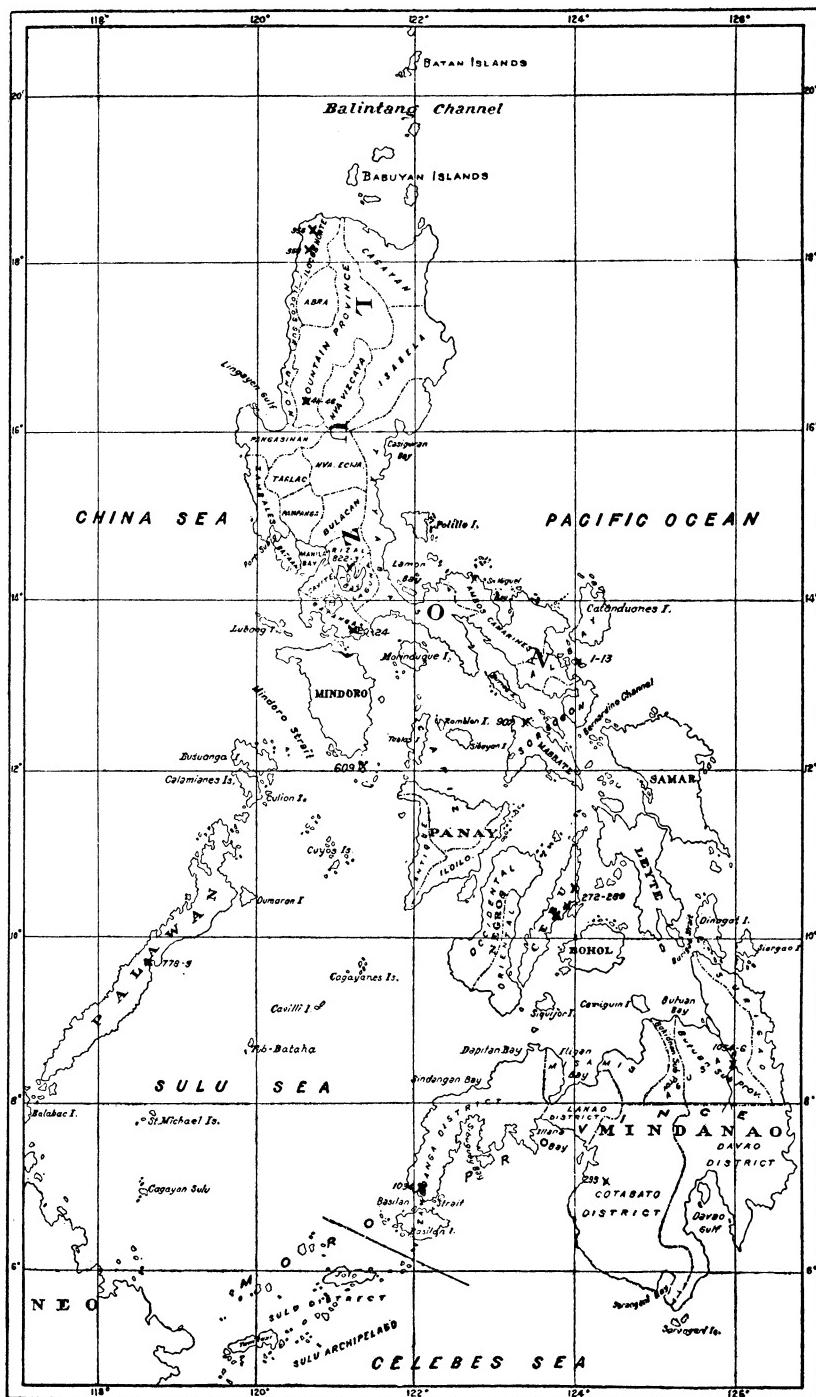
PLATE II.   THE PHILIPPINE ISLANDS SHOWING FOSSIL LOCALITIES.
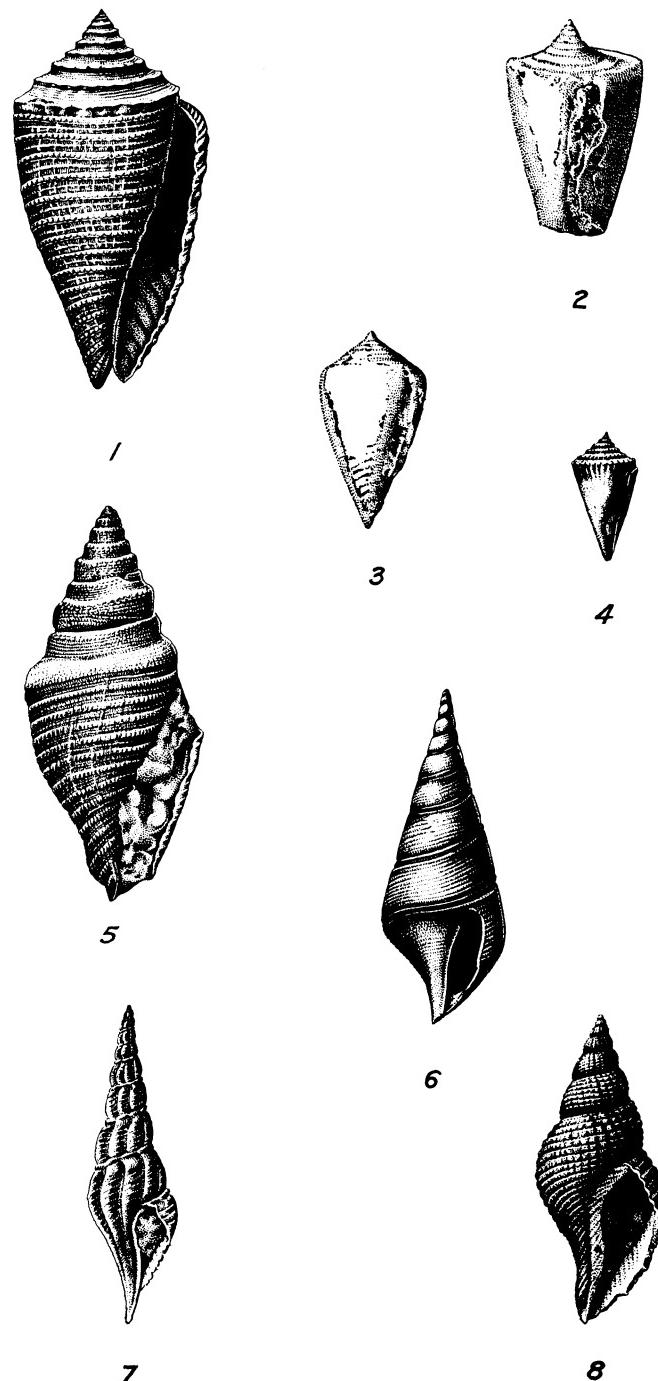
PLATE III.

Fig. 1. Conus sulcatus Brug. var. philippinensis var. nov.   2. Conus odengensis K. Mart.   3. Conus djarianensis K. Mart.   4. Conus sp.   5. Turris (Pleurotoma) andaensis sp. nov.   6. Turris (?) agusana sp. nov.   7. Turris flavidula Lam. var. sonde K. Mart.   8. Turbinella ilocana sp. nov.
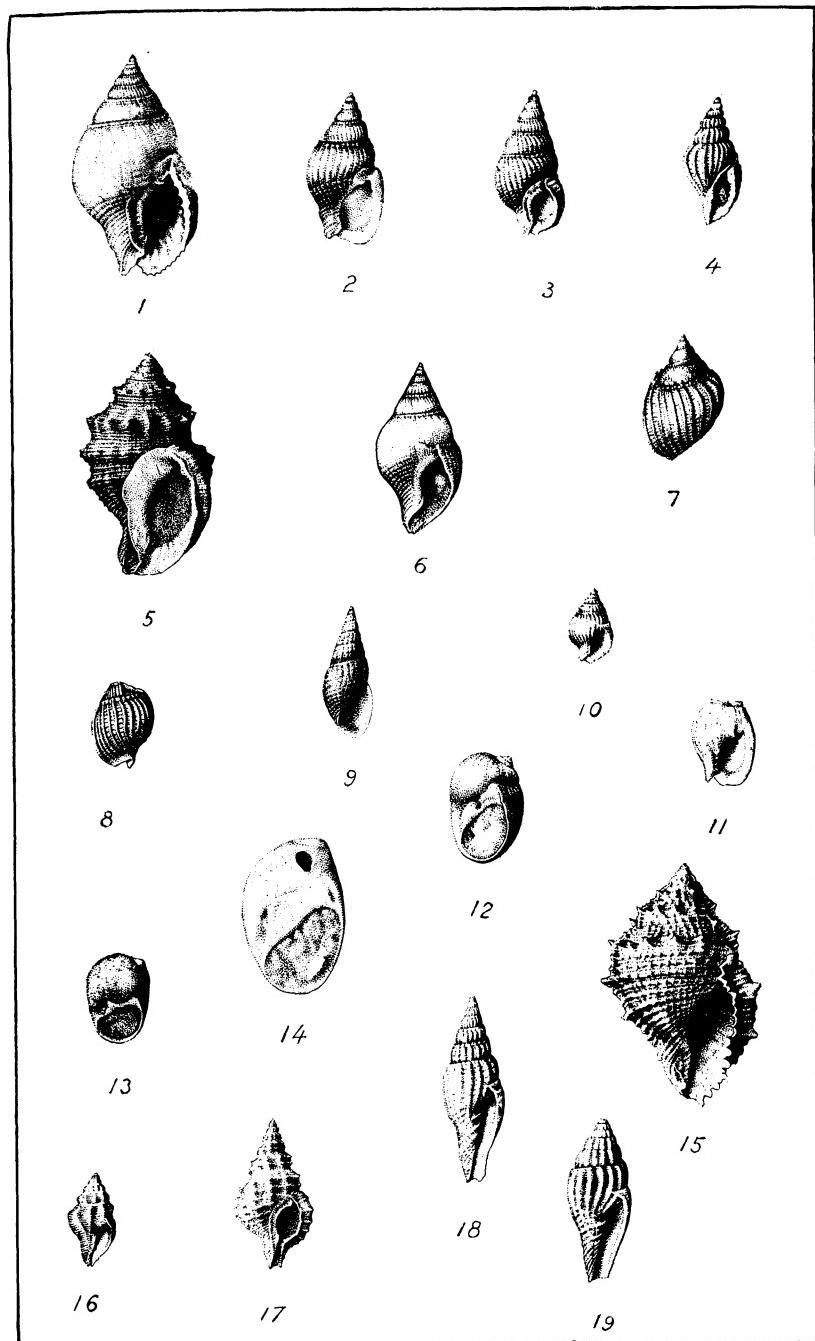
PLATE IV.

Fig. 1. Nassa caniculata Lamarck. 3. Nassa siquijorensis A. Adams. 4. Rimella javana K. Mart. 5. Cassidaria echinophora Linn. (?) 6. Nassa caniculata Lamarck. 2, 7, 8. Nassa verbeeki K. Mart. 9. Melanea laterita Lea. 10. Nassa verbeeki. 11. Nassa sp. indet. 12. Natica globosa Chem. 13. Natica (Lunatia) sp. 14. Polynices (Natica) mamilla Lam. 15. Bursa (Ranella) subgranosa Beck. 16. Tritonidea ventriosa K. Mart. 17. Hindsia dijki K. Mart. 18. Turricula jonkeri K. Mart. 19. Turricula bataviana K. Mart.
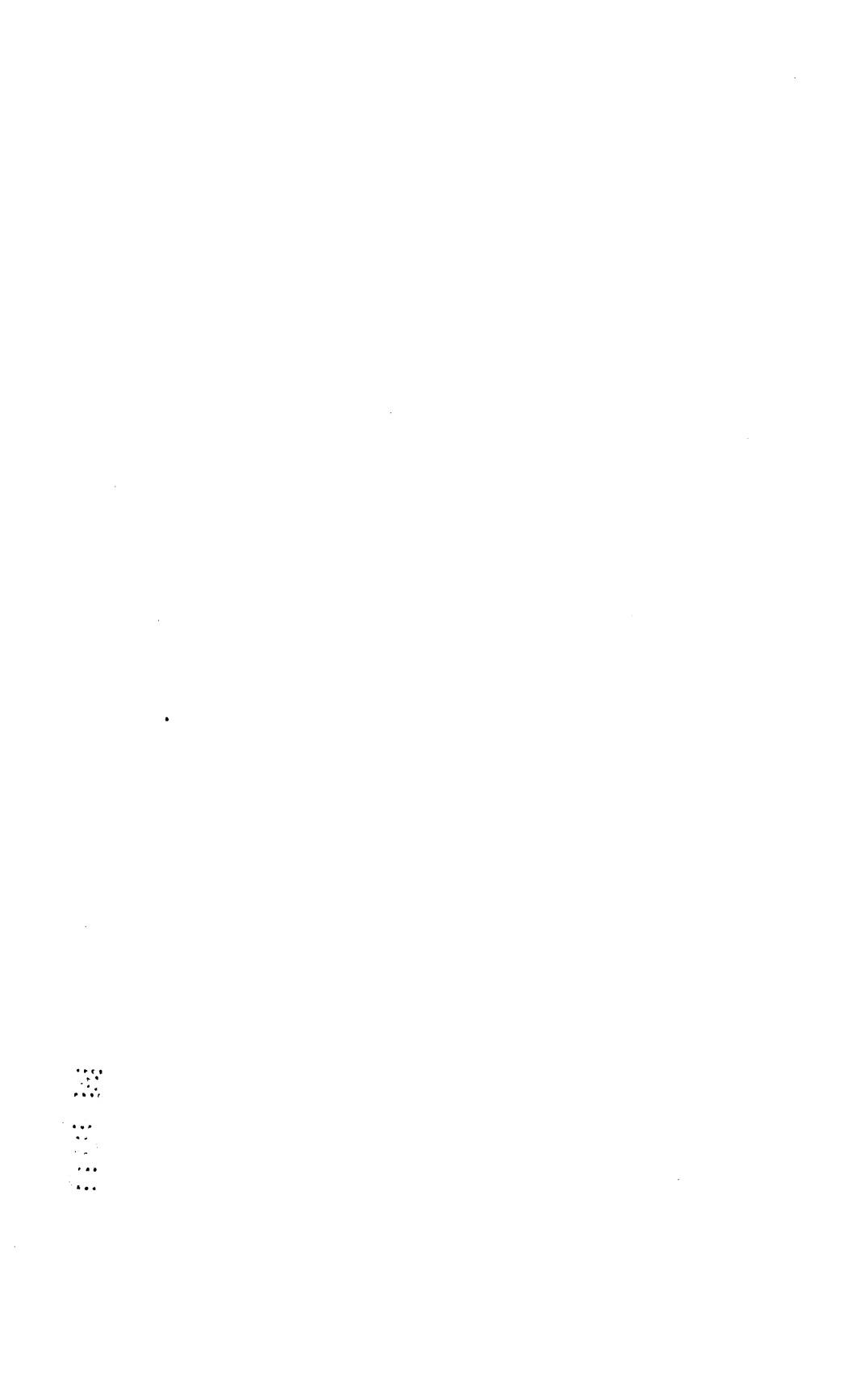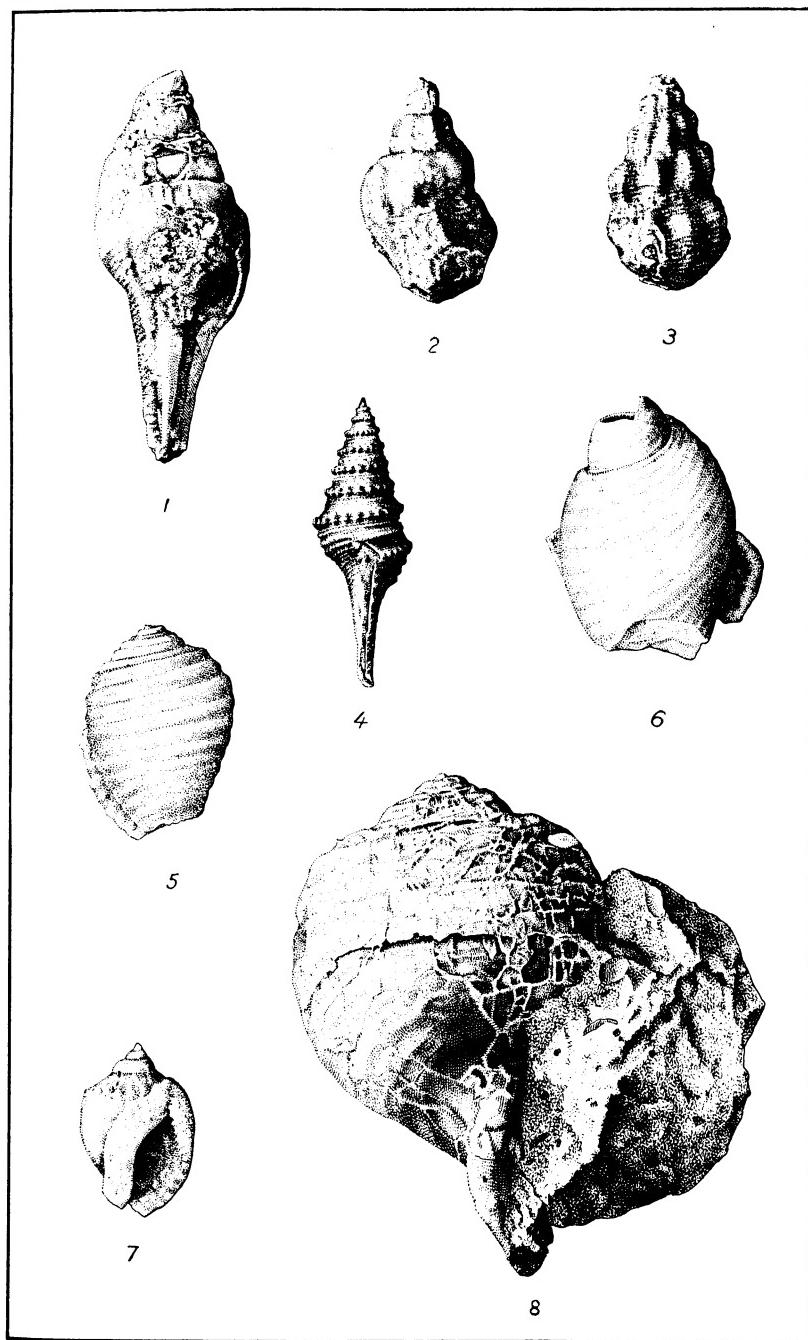
PLATE V.

Fig. 1–3. Turbinella tjidamarensis K. Mart. 4. Turris carinata Gray var. woodwarJi. 5. Dolium costatum Menke. 6. Cassis pila Reeve. 7. Cassis nodulosa Gmelin. 8. Dolium costatum Menke.
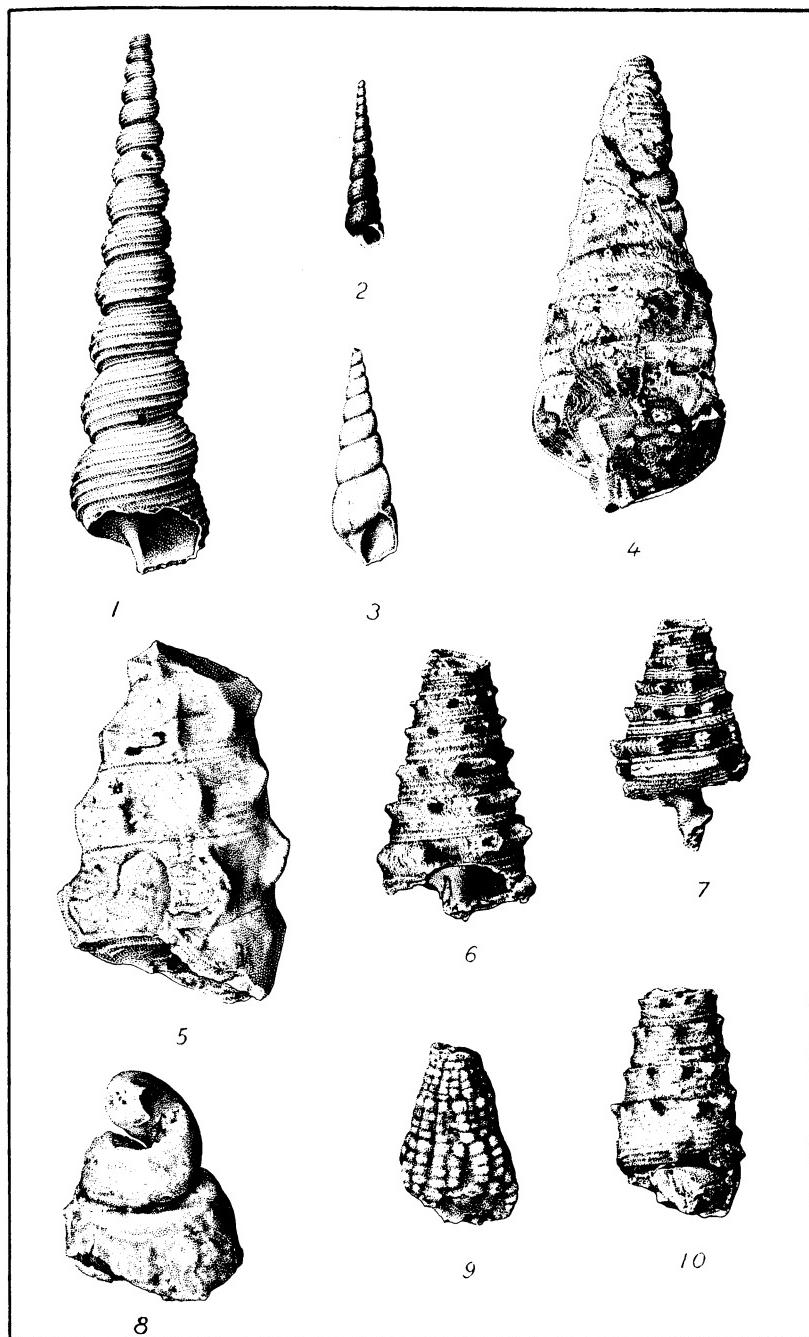
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Fig. 1. Turritella terebra Lam. 2. Turritella cingulifera Sow. 3. Melania woodwardi K. Mart.
4. Vicarya callosa Jenk. var. semperi Smith. 5. Cerithium (Campanile) sp. 6, 7. Vicarya
callosa Jenk. var. semperi Smith. 8. Vicarya callosa Jenk. var. semperi Smith, internal cast.
9. Cerithium (Potamides) palustris Linn. 10. Vicarya callosa Jenk.
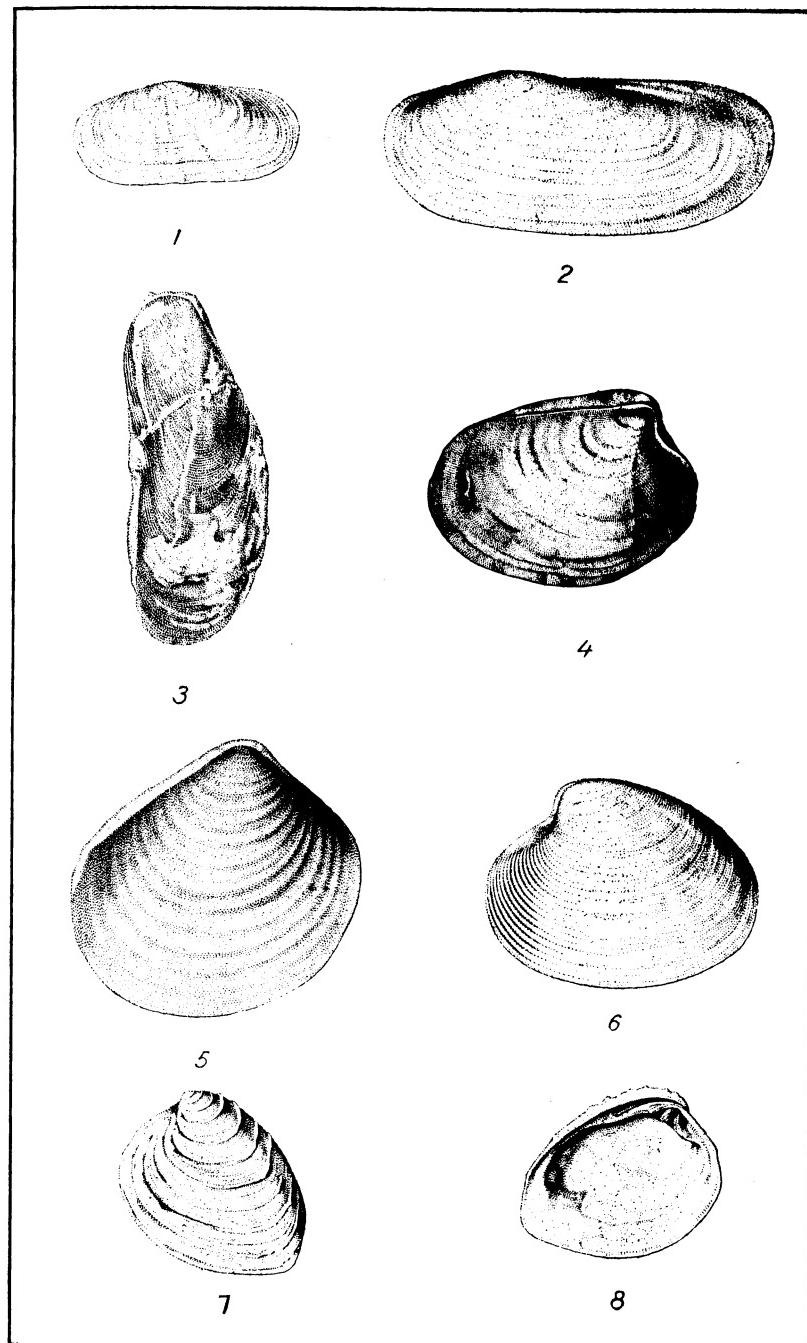
PLATE VII.

Fig. 1. Azor coarctatus Gmelin. 2. Cultellus maximus Gmelin. 3. Modiolus sp. 4. Clementia sp. 5. Clementia papyracea Gray. 6. Macrocallista ventricola K. Mart. (?) 7. Chione chlorotica Phil. 8. Chione chlorotica Phil., interior.
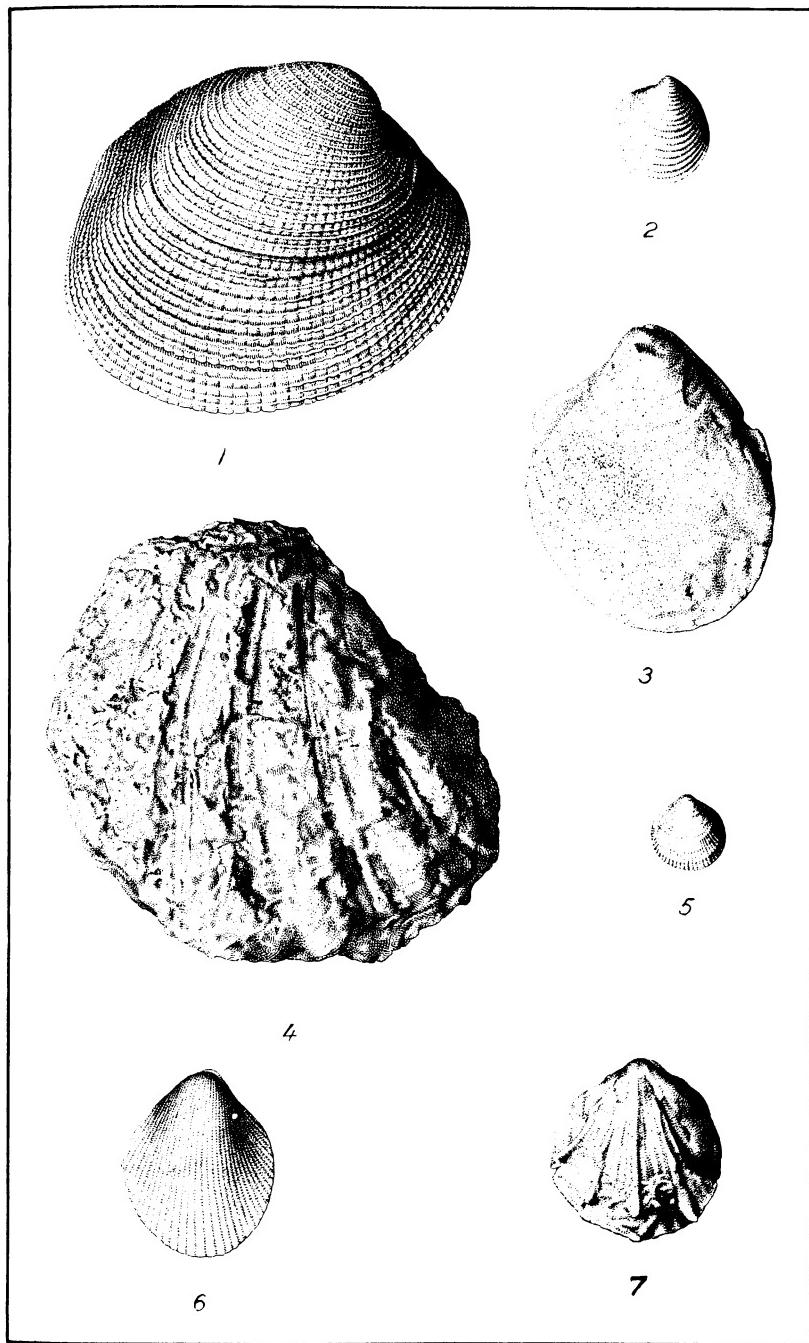
PLATE VIII.

Fig. 1. Chione (Venus) pulcherrima K. Mart.   2. Dosinia boettgeri K. Mart.   3. Clementia (?), internal cast.   4. Indeterminate, cf. Chlamys (Æquipecten).   5. Lucina sp.   6. Cardium elongatum Brug.   7. Spondylus sp., internal cast.
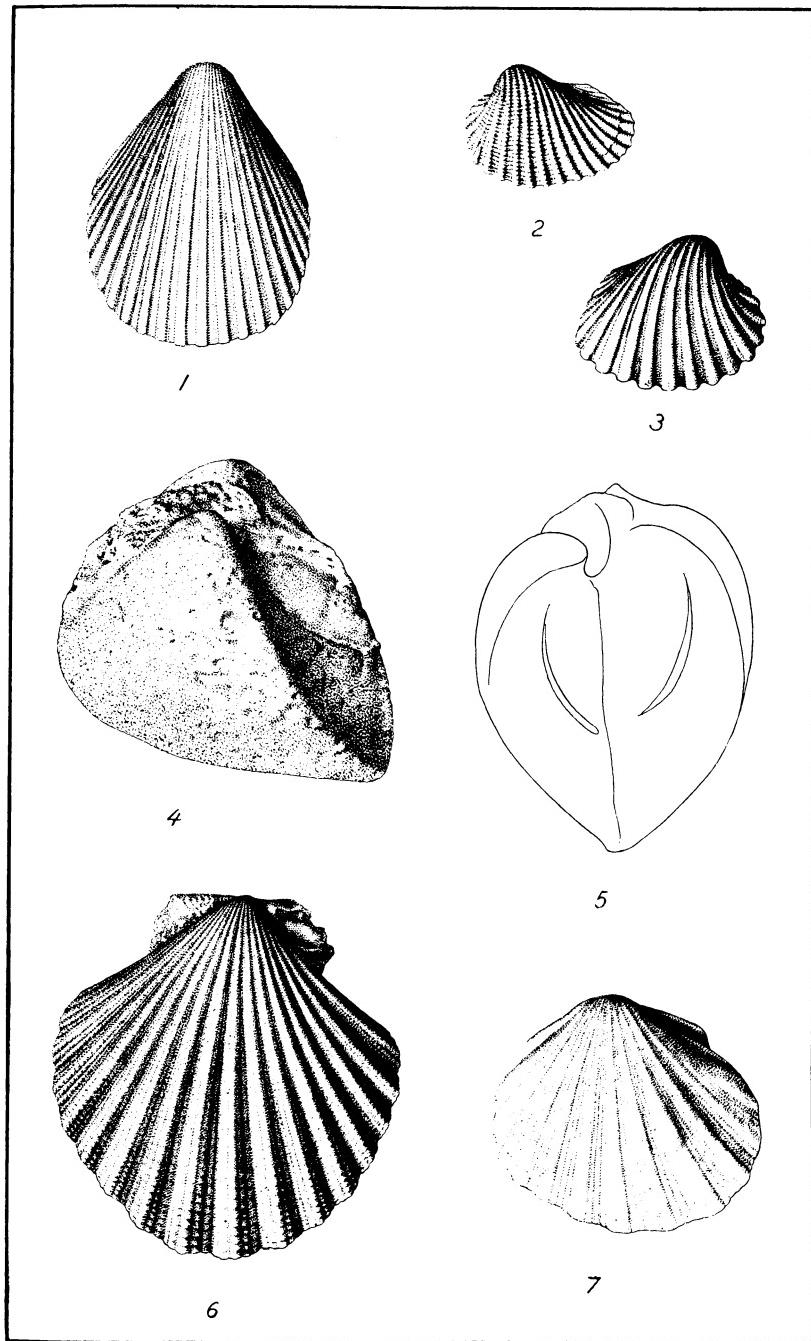
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   Reeve.   7. Pecten sulcatus Müll.
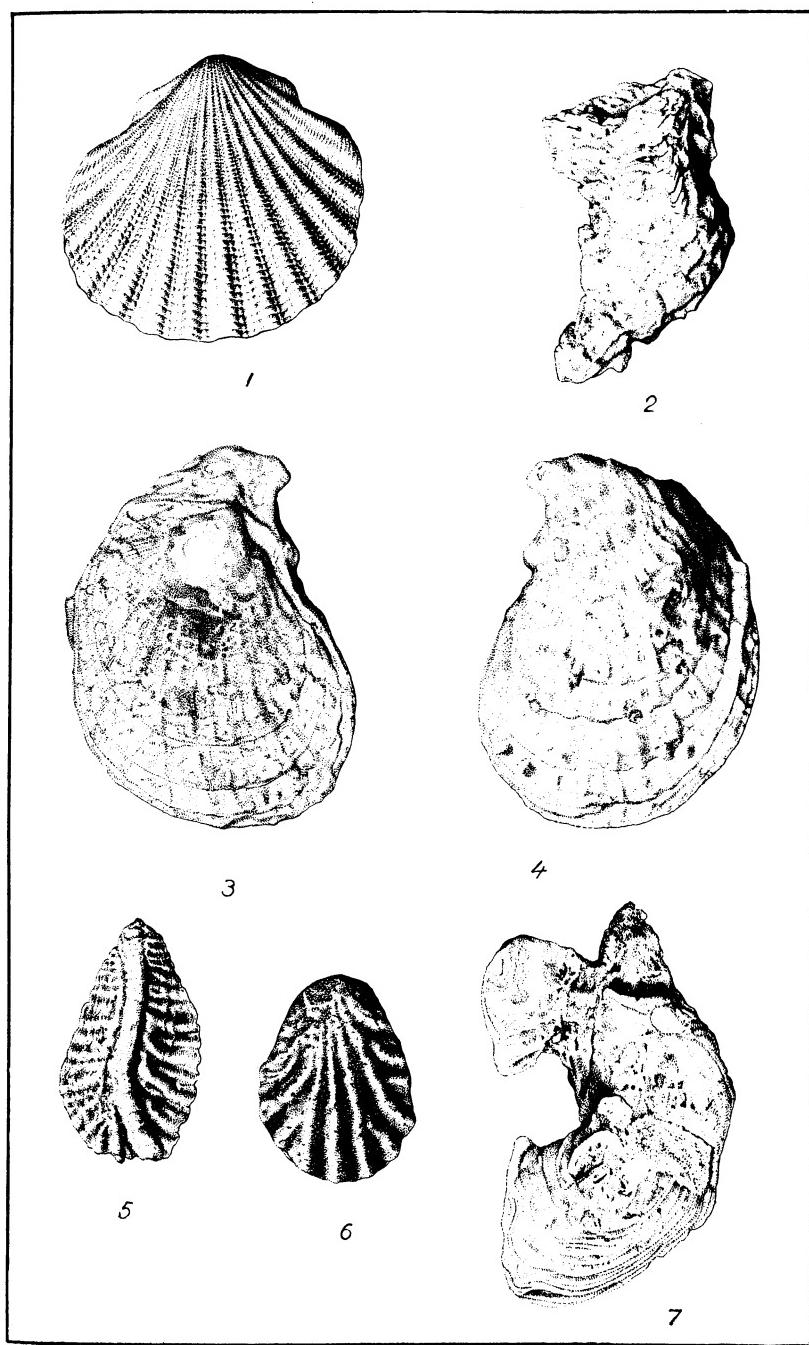
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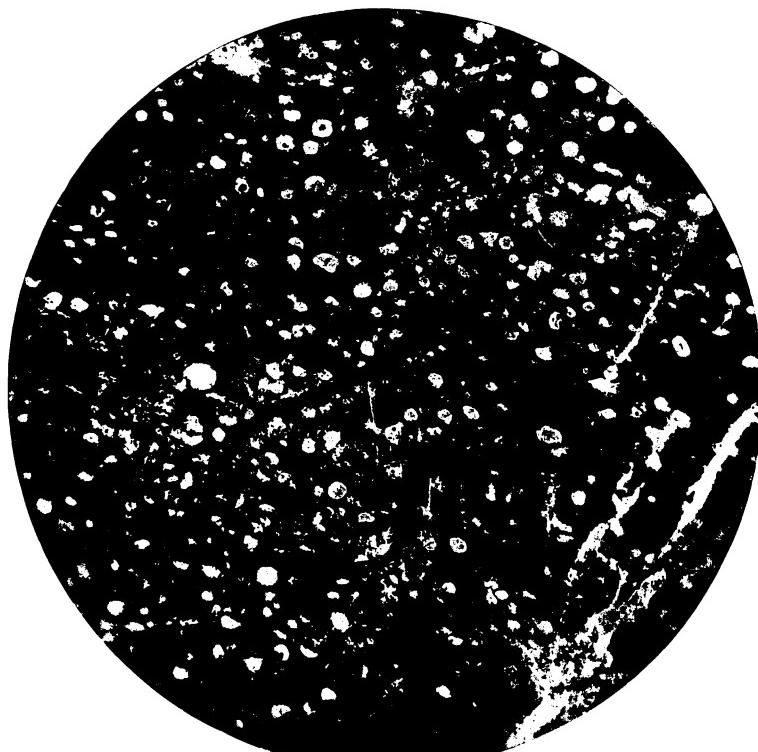
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Fig. 2.   Foraminiferal limestone, Batan Island.
PLATE XII.
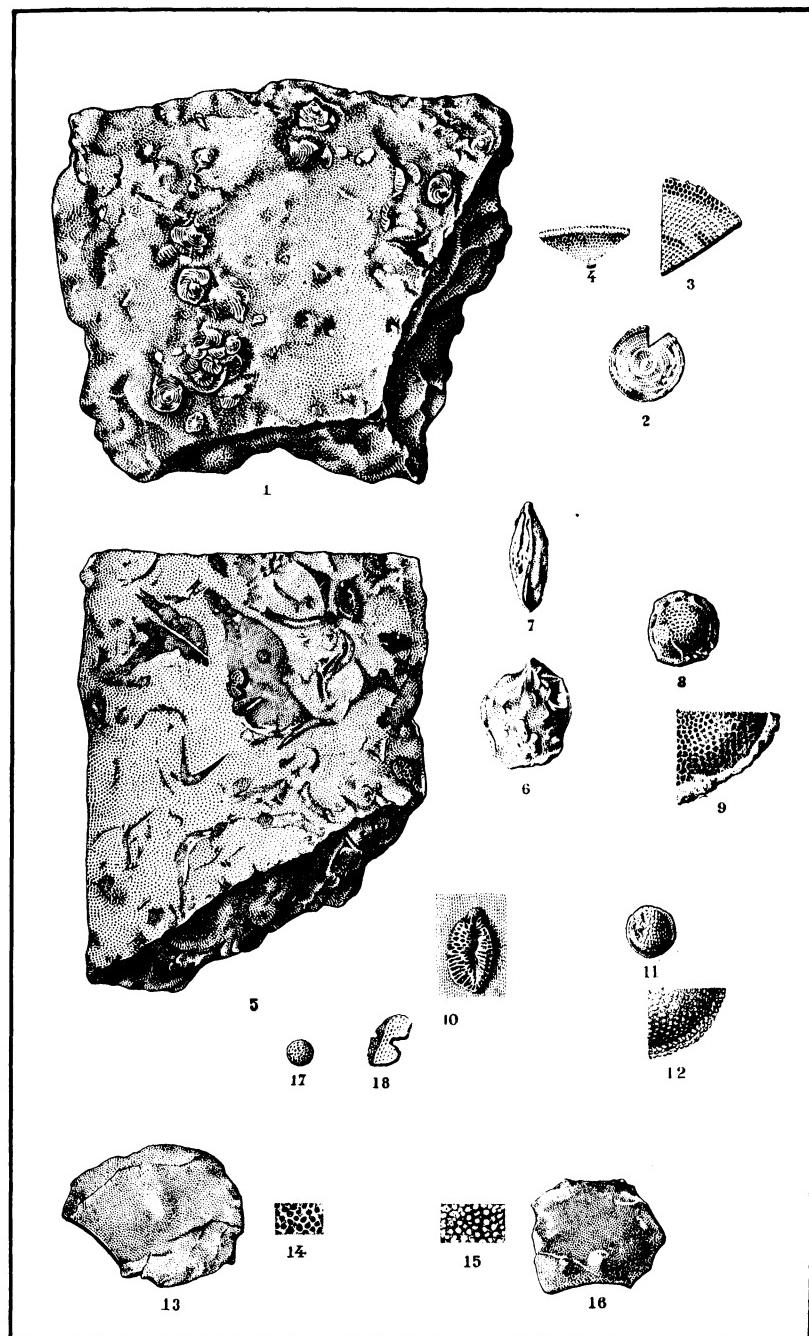
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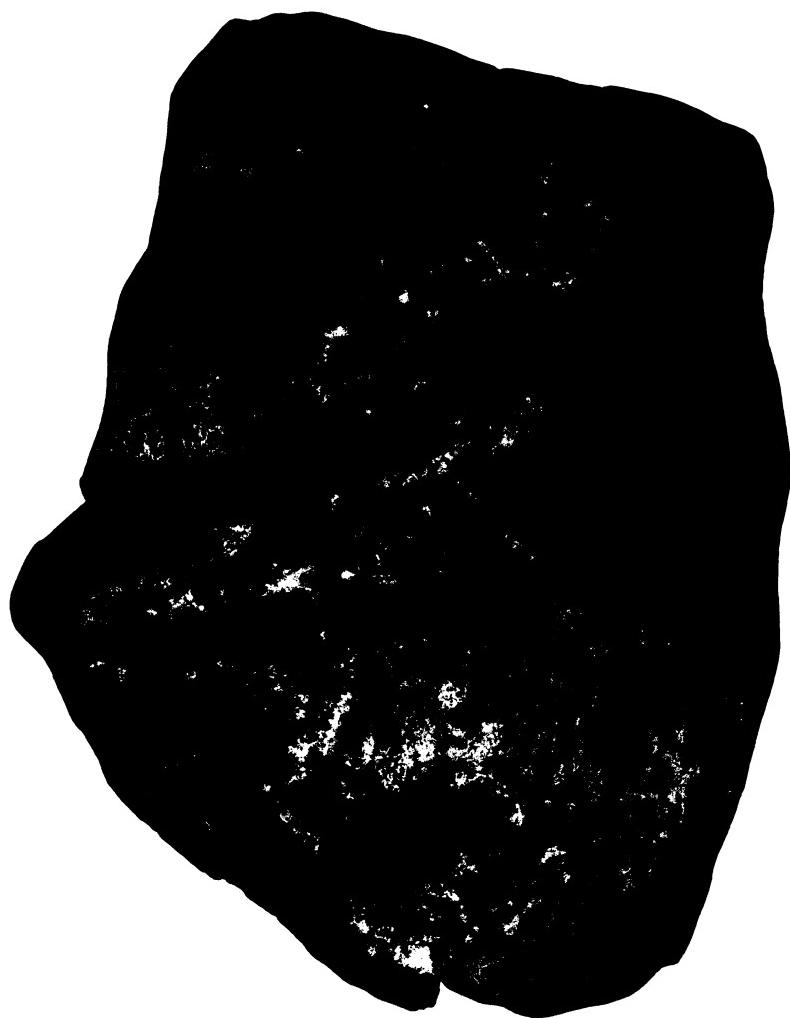
PLATE XIV. PYRULA (MELONGENA) SP. INDET.

Figs. 1-3.   Voluta sp. indet.
PLATE XV.

PLATE XVI.   TRIDACNA GIGAS LAMARCK.
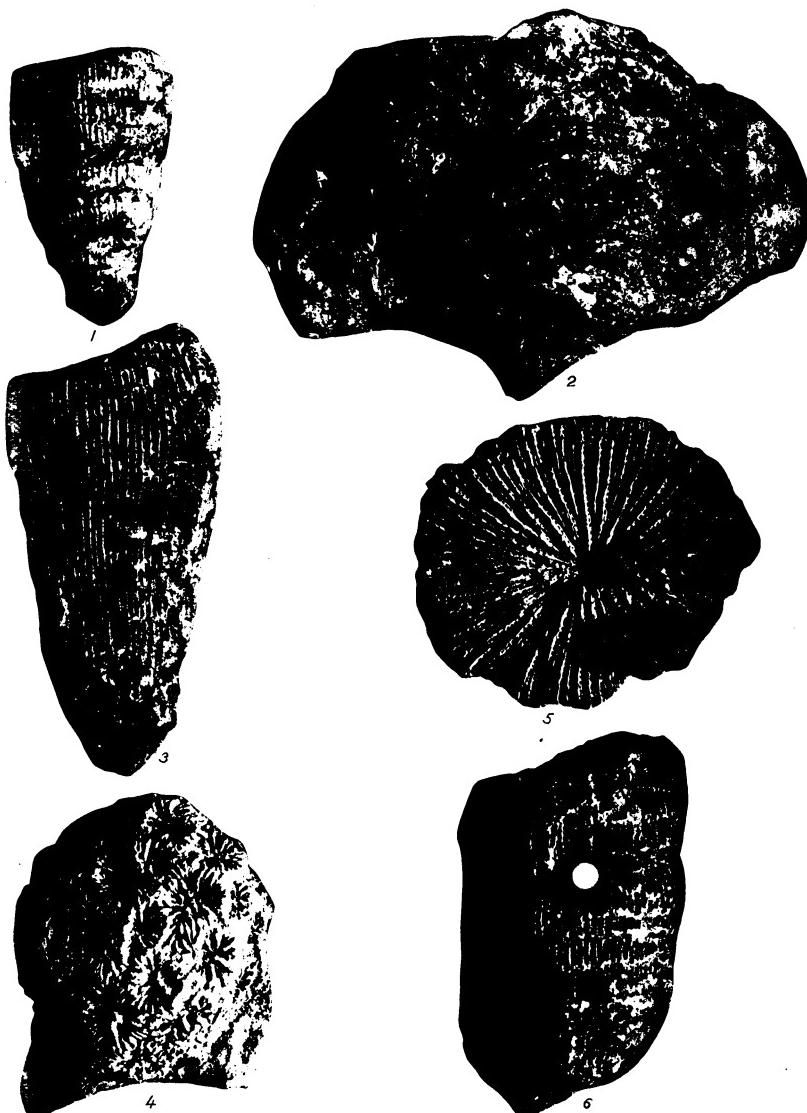
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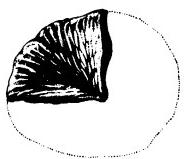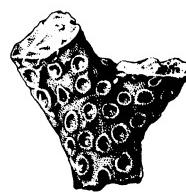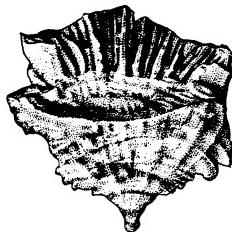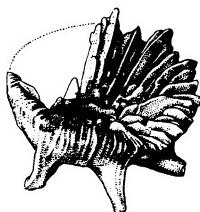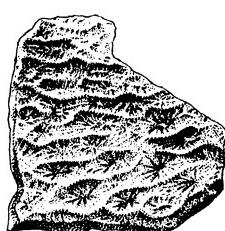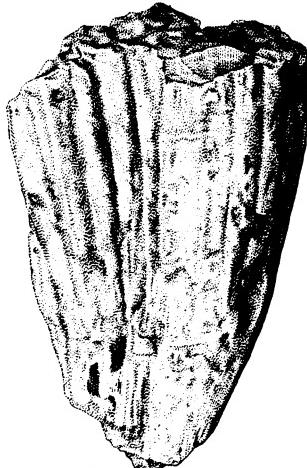
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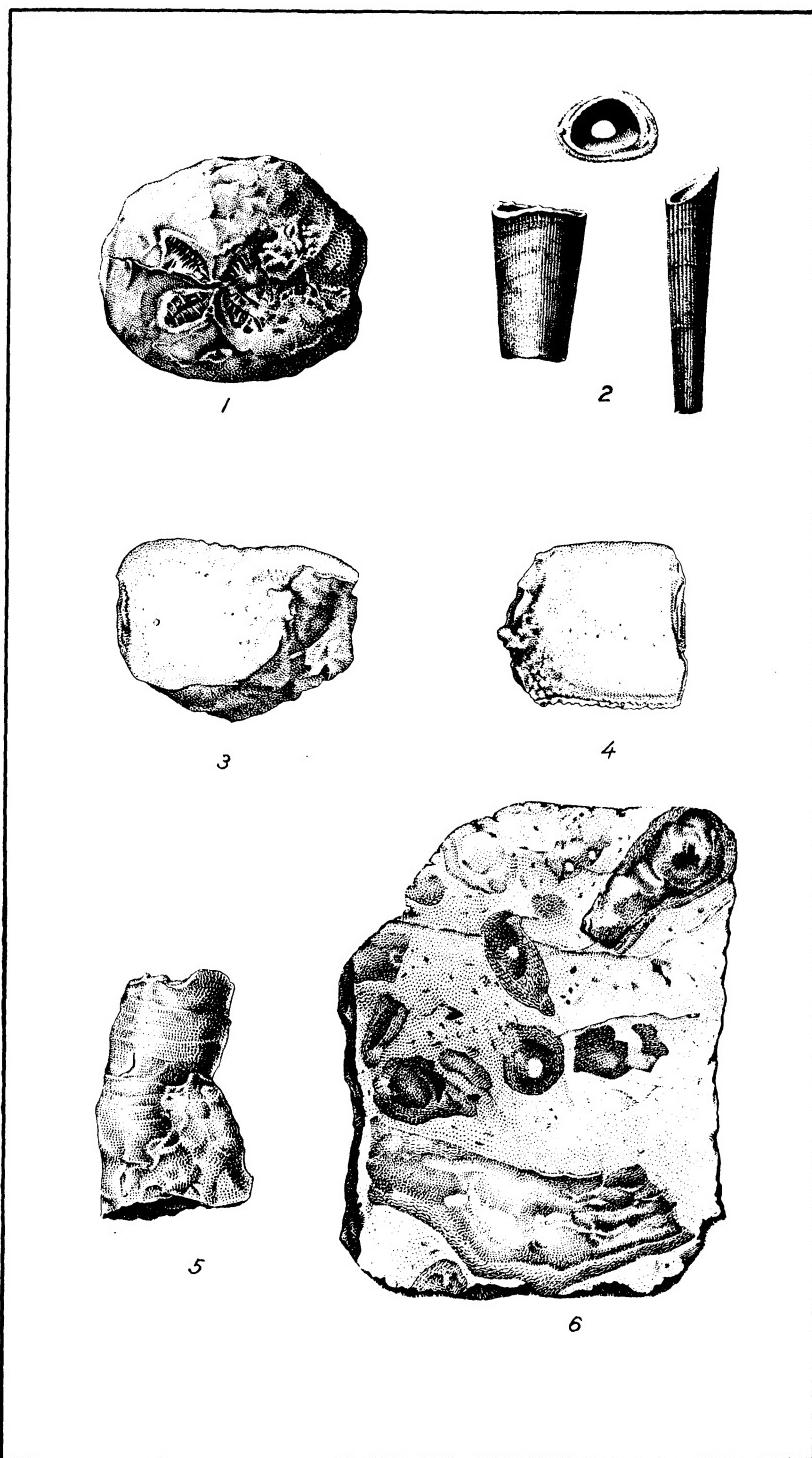
PLATE XIX.

Fig. 1. Schizaster subrhomboidalis Herkl.   2. Dentalium tumidum sp. nov.   3, 4. Callianassa
    dijki K. Mart.   5. Vermetus giganteus K. Mart.   6. Hydroid zoöphytes (?) in limestone
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Fig. 1. Section of old "slate" (?) containing Radiolaria. × 100.
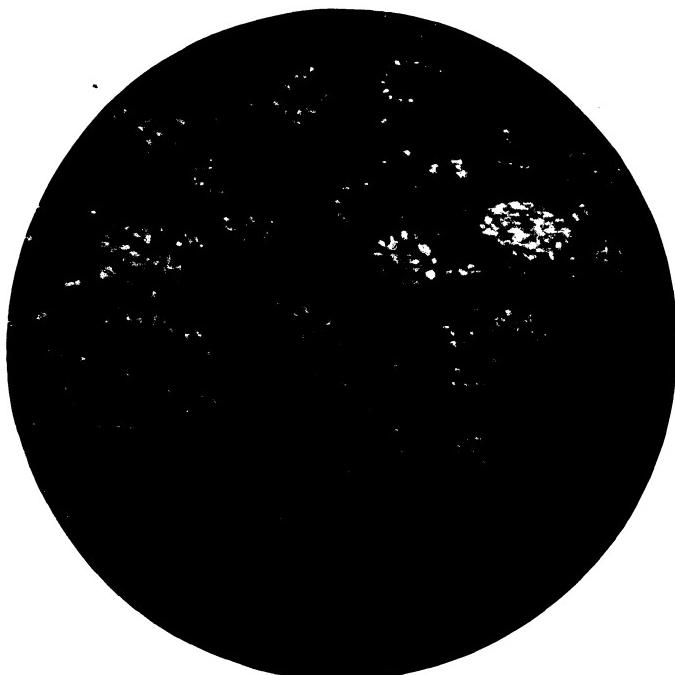
Fig. 2. The same specimen as that in fig. 1. × 200.

PLATE XX.

THE GEOLOGY AND PETROLEUM RESOURCES OF THE SOUTH-ERN PART OF BONDOC PENINSULA, TAYABAS PROVINCE, P. I.

By WALLACE E. PRATT AND WARREN D. SMITH

(*From the Division of Mines, Bureau of Science, Manila, P. I.*)

Ten plates, 1 text figure, and 1 map

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INTRODUCTION

GENERAL

The existence of petroleum seeps on the lower end of Bondoc Peninsula, especially on Bahay River, was known among the natives at least, during the Spanish régime, but no steps were

taken to explore the region, and no mention of petroleum in Tayabas is found in the records of the Spanish mining bureau. Soon after American occupation, however, prospectors reported oil from Bondoc Peninsula, and the field began to receive attention. E. W. McDaniel, S. W. Tilden, and the late Olney Bondourant were among the earliest prospectors to locate petroleum placer claims in Tayabas. Samples of the petroleum were submitted to the Bureau of Government Laboratories (now Bureau of Science) in 1903.

A shallow well was sunk on Bahay River in 1906 by the Tayabas Mutual Oil Association, with E. W. McDaniel as managing director. It is stated that 46 gallons of oil were obtained from this well in one day. The well was sunk "to a depth of 127 feet using a $3\frac{3}{4}$ by $2\frac{1}{2}$ inch by 3-foot bit operated by a hand power springpole and duplex block attachment." Another well, 23 meters deep, was sunk on Malipa Creek by Mr. E. J. Cooke and likewise is reported to have encountered oil.

Gradually, business firms in Manila became interested in the field, and the area over which claims were located constantly grew larger. Castle Bros. Wolf & Sons (now Pacific Commercial Company) acquired a number of claims on Bahay River, and, about the time of the publication by the Bureau of Science of a report [1] on the physical and chemical nature of the petroleum from the well drilled by Mr. McDaniel, this firm organized the Bahay Valley Oil Company and started to sink a deep well. The new well (Bahay 2) was located on Bahay River within 50 meters of the old well (Bahay 1), and was drilled by Mr. O. A. Leary. The well reached a depth of less than 100 meters, and obtained no more oil than the old well.

With the beginning of drilling by the Bahay Valley Oil Company, in 1910, interest in the Tayabas field reached fever heat, and claims were staked far and wide, but no further exploration was undertaken. Since that time most of the locators have merely awaited developments.

PREVIOUS KNOWLEDGE OF THE REGION AND SOURCES OF INFORMATION

The earliest published reference to petroleum in Tayabas is an anonymous article [2] dealing with the activity of the Tayabas Mutual Oil Association in 1906. A short discussion of the occurrence of petroleum in the Philippines by Smith [3] contains

[1] Richmond, Geo. F., *This Journal, Sec.* A (1910), **5**, 1.

[2] Oil fields of Tayabas, *Far Eastern Rev.* (1906), **3**, 102.

[3] *Ibid.* (1907), **3**, 9.

a general statement concerning Bondoc Peninsula. Later in the same year another article[4] on the Tayabas oil fields was published.

Richmond's[5] investigation of the physical and chemical properties of several samples from Bahay 1 well was cited above. Geo. I. Adams, formerly a geologist in the Bureau of Science, spent two weeks on Bondoc Peninsula in 1909, and his observations were included in a geologic reconnaissance of southeastern Luzon,[6] together with the results of a few days additional field work by the authors of that paper.

In January, 1911, F. T. Eddingfield and Wallace E. Pratt spent two weeks in a geologic investigation of the southern part of Bondoc Peninsula, and a short discussion based on this work was published later in that year.[7]

During the summer of 1912, Wallace E. Pratt and F. A. Dalburg were engaged for nearly three months in geologic and topographic field work on Bondoc Peninsula. The results of this work were confirmed and amplified in three weeks of field work by Warren D. Smith and Wallace E. Pratt in February, 1913. These two periods of field work constitute the basis of this report, although the results of previous field work have been drawn upon freely and have facilitated the work.

<div align="center">SCOPE OF THE PRESENT WORK</div>

The time spent in the field would scarcely permit of the detailed study of the area covered—700 square kilometers—even if the country were easily traversed and the geology clearly defined. As it is, the lack of an accurate map, the absence of trails, the prevalence of jungle along the streams, and the heavy growth of cogon and *talahib*[8] have made it impossible to include detailed or complete information in this report. The vegetation usually conceals the geologic relations, and often renders impossible a proper examination of places where precise information is important. The mere physical effort of cutting through a jungle or of "breaking trail" in the open, where the process involved is one of literally burrowing through the tall rank grass, fre-

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[4] *Ibid.* (1907), 4, 19.

[5] *Loc. cit.*

[6] Adams, Geo. I., and Pratt, Wallace E., *This Journal, Sec. A* (1911), 6, 473. Adams's report also appeared as Bureau of Science press bulletin 2 which was printed in *Philippine Resources* (1909), 1, 19, together with The Oilfields of Tayabas, a descriptive article by H. C. Hosty.

[7] Eddingfield, F. T., *Min. Resources P. I. for 1910*, Bur. Sci. (1911) 64.

[8] Cogon, *Imperata cylindrica* Beauv.; talahib, *Saccharum spontaneum* Linn.

quently leaves the observer inefficient through exhaustion before his day's work is fairly begun.

If the petroleum resources are developed, it is anticipated that the additional and more accurate data which will become available as the jungle is cleared away and deep wells are drilled will modify, or perhaps reverse, some of the conclusions of this preliminary report. However, the present work should serve as a basis for future investigation.

<div align="center">METHODS OF FIELD WORK</div>

Field work on Bondoc Peninsula requires complete camp equipment and the importation of all supplies from Manila. Moving camp—a frequent task because of the limited area to which operations from each center are necessarily confined—involves packing everything on the backs of carriers, except along the coast where small boats can be employed. The carabao, which is used to a small extent as a pack animal by the native, is not efficient in the interior, because water in quantity for its requirements is not usually available.

The geologic and topographic mapping, which is embodied in the map accompanying this report, was executed in large part with improved compasses, known as pocket transits, during the main period of field work. The coast line and the elevations of the principal points, the altitudes of which could be determined by triangulation from the sea, are taken from a coast survey by the Bureau of Coast and Geodetic Survey. Upon this base is plotted a triangulation survey which established the relative locations of a number of points between Mount Maglihi and Mount Cambagaco, made by Mr. Dalburg, using a standard surveying transit. A stadia traverse by Mr. W. D. Buxton, of the Bureau of Lands, from the town of Bondoc, via Bacau, to the mouth of Bahay River and the small number of public land surveys in the region are likewise included. For the rest, compass surveys along the principal trails and stream lines—the distances being paced—with vertical angle calculations and aneroid barometer readings for elevations were made to serve.

The measurements and observations involved in defining the stratigraphy and the geologic structure were made a part of the compass traverses, data of this sort being most readily obtained along water courses. It is recognized that the reliability of stratigraphic and structural determinations made from measurements along streams has been questioned by eminent geologists, and the objection may be admitted, but the fact remains that usually in the tropics the only clue to the nature of the rocks beneath the surface débris is to be obtained in the streams.

Even in stream beds, geological observations are generally confined to sections where active erosion is in progress. Where limestone forms a part of the rock series, as in Tayabas, the universal deposition of travertine by flowing water is another factor which tends to conceal the geologic relations.

The best criterion of the degree of accuracy which should be accorded to this report is to be gained from a consideration of the relative precision of the field methods employed. In one sense, the closely determined elevations usually required for the proper correlation of deep-well records were not essential to this preliminary work in as much as no deep wells have been drilled in the area described. Owing to the lack of deep wells, on the other hand, the degree of conformity between surface and underground strata in their structural relations and thicknesses is unknown, and the structure recorded may not be that of the deep-lying formations.

GEOGRAPHY

The established native usage is followed in this paper for place names, the names of natural features, rivers, mountains, etc. Where words have been passed upon by the United States Geographic Board, the accepted spelling is adopted.

SITUATION

The area over which oil seeps are known to occur in Tayabas, as shown on the accompanying map, includes that part of Bondoc Peninsula south of the towns of Catanauan and San Narciso, or approximately the southern half of the peninsula. The territory mapped has an average width of 17 kilometers, is 50 kilometers long, and contains an area of 700 square kilometers. Bondoc Peninsula marks the southern termination of the Eastern Cordillera of Luzon. It is a long, narrow strip of land protruding to the south-southeast from the southern coast of the mainland of Luzon. The parallel of 13 degrees and 30 minutes of north latitude and the meridian of 122 degrees and 30 minutes of east longitude pass through the region in which the oil seeps occur. The principal towns at which steamers touch, Catanauan and Mulanay on the west coast, are about 320 kilometers (sailing distance) from Manila. The position of Bondoc Peninsula with reference to the other parts of the Philippine Archipelago is shown on the index map.

TRANSPORTATION

The only access to the lower part of Bondoc Peninsula at present is by steamship. Several small boats touch at Catanauan irregularly, averaging once a week, while the same boats

stop at Mulanay somewhat less frequently.   The nearest railroad station is at Lucena, about 70 kilometers northeast of Catanauan.   None of the rivers in the oil field are navigable.   No improved roads have been built on the peninsula; there are poor trails between Catanauan and Mulanay, Mulanay and San Narciso, Mulanay and Bondoc, and between Bondoc and San Andres. A few of the smaller outlying villages are connected by trails, but these are used so little that they are not kept open and are generally hard to follow.   The principal trails are indicated on the map.

CLIMATE AND VEGETATION

The months of March, April, and May constitute the dry season, and are the best months for field work on the peninsula. The rains begin in June, and continue regularly through July and August.   During the other months of the year the rainfall is intermediate between that of the dry season and that of the wet season.   The Weather Bureau has no station in this region, and consequently exact meteorologic data are not available.

The more precipitous valleys and the mountainous regions are wooded.   Parts of the woods are good forest and fairly open, but a large area has been cut over by the natives and is now an impassible jungle of undergrowth.   The country of intermediate elevation is usually not wooded, but is covered with a rank growth of cogon.   Mangrove swamps are encountered near the mouths of some of the rivers and on other areas of low ground along the coasts.

POPULATION

In 1903 the total population in the area shown on the map was 10,088.   More than 40 per cent of this number lived in the municipality of Catanauan.   Bondoc and San Narciso, which were listed as municipalities in the census of 1903, subsequently fell to the rank of barrios, although the latter again has been made a municipality within the last year.   The population is little if any greater, and it may be slightly less, than in 1903.

Coconut growing is the main resource of the region.   Small herds of cattle are encountered in the interior, but the number is far less than the available grazing territory could support. There are limited areas suitable for the cultivation of rice at a number of places, but here again the opportunity is not generally improved.   A natural asset of the country is the buri palm which grows without cultivation everywhere.   From it the native secures the material for his house and for the manufacture of mats and bags—a household industry.   His shoes are of buri

bark, and in times of want the wood of the tree is ground into buri flour which feeds his family.

It may be anticipated that labor will be scarce should this field become active and that the efficiency of the local supply will be low.

GEOLOGY

GENERAL STATEMENT

Bondoc Peninsula is made up almost entirely of sedimentary rocks, and, if the regions of more recent sedimentary material, such as the alluvium and raised shore deposits of the central plain of Luzon and the volcanic tuff of southwestern Luzon, be excepted, is one of the largest areas in the Philippines where the rocks are essentially sedimentary and not seriously affected by intrusion or vulcanism.

The series is principally shale and sandstone, with subordinate thicknesses of limestone in the higher portion. The youngest beds, disregarding the recent unconformable deposits, are Pliocene limestones, while the oldest rocks encountered are lower Miocene or Oligocene shales. The measured sections show an aggregate thickness of from 1,700 to 1,800 meters, and the base of the shale series is not exposed. Possible repetition of beds through minor faulting may make the apparent thickness greater than the actual. The strata have been forced into folds along lines trending approximately parallel to the axis of the peninsula; namely, north-northwest and south-southeast. The folding has resulted in a principal anticline along the central portion of the peninsula, separated by wide shallow synclines from subordinate, more or less parallel, anticlines near the coasts on each side. This simple structure is complicated by the presence of minor folds approximately at right angles to the general trend. The limestone at the top of the series has been folded in general conformity with the lowest shale, so that the major lines of structure are common to the entire stratigraphic column. The anticlines of the folds are sharp, but the occurrence of extensive faulting is not established.

PHYSIOGRAPHY

Excluding San Narciso Peninsula, the lower part of Bondoc Peninsula may be considered as a single geographic and orographic province. The outline is regular, with the lateral coast lines parallel, and the width maintained fairly constant to the extreme end. The coasts swing to the west as the southern end of the peninsula is approached, giving the southern portion of the field an almost north and south axis, while farther north

the axis trends north-northwest and south-southeast. Pusgo Bay, lying between San Narciso Peninsula and the mainland, is the largest coastal indentation. San Narciso Peninsula is remarkably similar in form and contour to the larger parent mass.

OROGRAPHY

The surface of Bondoc Peninsula rises from the seashore on both sides to a generally high, but dissected, interior. Before erosion became effective, the peninsula must have had a flattened, arch-like cross section. Through erosion, however, a great deal of the material of the former arch has been removed, the relative proportion which remains varying locally. In the northern part of the field, but little of the old surface is left—a ridge of tilted beds dipping toward the sea along the lateral coasts represents the lower part of the sides of the arch, while the highest elevations, farther inland, lie just below the former surface of the crown portion. Farther south erosion is not so far advanced and the larger part of the crown remains as a high interior plateau, incised by deep cañons.

From San Narciso south along the eastern coast the coastal ridge continues unbroken to the mouth of Vigo River, which cuts through it between the peaks of Cambagaco (elevation, 300 meters) on the north and Dagmit (elevation, 350 meters) on the south. South of Mount Dagmit, the ridge is continuous to Bahay River, which like the Vigo empties into the sea through a narrow steep-walled valley. South of Bahay River the crest of the ridge is broken by the valleys of several small streams which flow across it, and the elevation decreases; although Mount Maglihi, one of the southernmost peaks, is 390 meters high and is mountainous in aspect.

On the western coast, the marginal hills are lower (elevation, from 100 to 200 meters), the chain contains no conspicuous peaks, and the ridge is generally less prominent than the eastern coastal ridge.

In the central portion of the peninsula, the dissected plateau is formed by Cudiapi Range (highest elevation, 443 meters) on the north, with Balinsog Hill (elevation, 394 meters), Malumbang Plain (elevation, 250 to 270 meters), Mount Malasimbahan (elevation, 360 meters), Mount Anuing (elevation, 350 meters), Mount Banaba (elevation, 355 meters), and their environs making up the southeastern portion. South of Cudiapi Range and west of Mount Banaba, the high tableland persists across Pinamalijuan Plain to the vicinity of Tala and Sili. On the north this interior plateau drops abruptly to the low-lying valleys of

Matataja and Vigo Rivers and is separated from the coastal ridges on both sides by other erosional valleys. To the southeast the plateau is not perfectly detached from the coastal ridge, the intermediate valleys being shallow.

The southern termination of the interior plateau is at some distance from the seashore, and a strip of low ground, several kilometers wide, intervenes between it and Bondoc Head (elevation, 392 meters)—a conspicuous landmark for navigators rounding the southern point of the peninsula.

Mount Maclayao, 398 meters in height, is the most prominent elevation in the north-central part of the field. It is really a part of the west coast ridge, although it extends eastward into the interior, and forms an area of high ground common to the headwaters of the main drainage systems north of the plateau region.

HYDROGRAPHY

The main streams debouching upon the lateral coasts are confined in comparatively narrow valleys near their mouths. Where erosion is well developed, their middle courses are meandering and are bordered by wide flat terraces of alluvium. The main lines of flow follow the trend of the peninsula, so that streams working back from the east and west coasts attain relatively short lengths in the direction of their lower courses, but develop their principal tributaries at right angles on each side, draining long strips of territory to the northwest and southeast. Vigo River, for example, flows almost east into the sea at its mouth; but its largest affluent, Malipa Creek, flows north for a distance greater than the length of the Vigo below the junction of the two. Tagatay River, or the upper part of the Vigo, flows southeast for a distance equal to the length of the lower east-flowing portion of the stream, and other large tributaries come into Vigo River from the northwest.

Pagsanhan and Talisay Rivers, which empty into the sea on the southern coast, flow throughout their lengths in comparatively straight lines. Talisay, or Malumbang River, and Silonguin, or Canguinsa River,[9] are remarkable in having no important tributaries. In the plateau region these rivers and the Amoguis branch of Pagsanhan River flow through narrow cañons. Bahay River also has a deeply eroded valley, but has developed large tributaries.

Ayoni, Matataha, and Mulanay Rivers are formed of several

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[9] In the native usage a river assumes the name applied to the locality through which it flows; consequently the same river may have several different names.

affluents of nearly equal importance which unite in one stream as they approach the western coast. The Ajus, farther north, is like the Vigo in the orientation of its branches. Guinhalinan River, which is one of the largest rivers on Bondoc Peninsula, consists of two principal tributaries coming together from almost exactly opposite directions. Its south fork heads in the northeastern part of the area mapped, and flows north-northwest for a distance of 15 kilometers where it meets the north fork, which comes an equal distance from the north-northwest. From the point of confluence the merged streams flow eastward into Ragay Gulf, a distance of 5 kilometers. Thus, the main drainage of Guinhalinan River is at right angles to the course of, and about six times as long as, the principal stream.

TOPOGRAPHIC CONTROL

The general alignment of the water courses parallel to the trend of the peninsula and the relatively short stream lines at right angles to this trend—an extreme example of which has been cited in the case of Guinhalinan River—are obviously due to the control exercised by the prevailing strike of the rock strata. Not only has the strike of the inclined beds affected in this manner the alignment of the rivers, but the structure has influenced the relative positions of the main valleys and uplands. Thus, the valleys find their greatest development in, or near, the crests of anticlines; while the higher elevations occur in synclinal troughs, on the limbs of the anticlines, or in regions where the folding has not been severe (see geologic sections).

The upper courses of Vigo, Matataha, and Canguinsa Rivers all lie in the crest portion of the Central anticline. The lower part of Vigo River has cut through the ridge bordering the east coast along the axis of a small anticline, and Silonguin River has followed a similar line of cross structure. At the mouth of Mulanay River, likewise, the beds strike east-northeast and are steeply inclined, although only the southern limb of this possible cross anticline has been proved. The high areas in Cudiapi Range and in Bondoc Head represent synclines, while the plateau to the south and southeast of Canguinsa River occupies a region which has not been greatly disturbed in the process of folding. The ridge on each of the lateral coasts consists of strata lying well down in the limbs of the general arch of the peninsula, with Mount Maclayao near the western coast, marking also the southern limb of the cross flexure at the mouth of Mulanay River.

It is believed that the processes which resulted in the folded condition of the strata were initiated prior to the emergence of

Bondoc Peninsula above sea level. Probably the elevation is due, in part at least, to the folding and the main folds were outlined in the original land surface. If this theory is correct, the early water courses must have occupied the structural troughs or synclines. As folding progressed the anticlines became very acute, and their position must have been marked by extensive local shattering of the nonyielding limestone and calcareous sandstone in the upper part of the stratigraphic column. The synclines, on the other hand, were left in broad gentle folds not sufficiently pronounced to break the strata. Obviously, these conditions would tend to hasten the progress of erosion along the anticlinal zones; valleys probably formed on the anticlines and developed with greater rapidity than was possible in the synclines. Consequently, the synclines were soon deprived of their streams through the piracy of the anticlinal drainage, and the translation of the main water courses from synclines to erosional valleys on the anticlines was accomplished.

There is a striking contrast between the low hills and wide valleys, which are found in regions where the soft shale in the lower part of the stratigraphic column has been exposed to erosion over large areas, and the steep-walled valleys and the general youthful appearance of the topography in parts of the field where the upper formations have been preserved. Once these protecting rocks are removed, the shale yields readily to the cutting action of the run-off and relatively mature land forms result.

It is probable that rivers emptying into the sea upon the lateral coasts and gradually working inland along the lines of cross structure have captured drainage, which previously had followed the general strike of the formations. An apparent example of a stream so captured is Canguinsa River, which probably at one time flowed south into Amoguis River.

STRATIGRAPHY

Table of stratigraphy.—Table I shows the stratigraphic and age relations of the rocks in the area under discussion. Tables II and III with similar data for the largest producing oil fields near the Philippine Archipelago are inserted for comparison.[10] Table II represents the Echigo field in Japan, and Table III[11] the Moera Enim field in southern Sumatra.

[10] Iki, Tounenaka, Preliminary notes on the geology of the Echigo oil field, *Mem. Imp. Geol. Surv. Japan* (1910), No. 2, 29.

[11] Tobler, Aug., Topographische und Geologische Beschreibung der Petroleum Gebiete bei Moera Enim (Süd Sumatra). Tidschrift van het Kominklijk Nederlandsch Aardrijkskundig Genootschap. (1906) Tweede Serie, 23, No. 2, 199.

TABLE I.—*Provisional scheme of stratigraphy. Bondoc Peninsula, Tayabas.*

Series.	Formation.	Subdivisions and character.	Thickness.	Characteristic fossils.	Geologic condition of deposition.
			Meters.		
Recent	Alluvium	Clay, sand, gravel, and travertine	0–10		Fluviatile.
Pleistocene and Recent	Coral reefs and littoral deposits.	Raised coral reefs, beaches, etc	0–15		Seashore deposits during slow elevation.
Unconformity					
Pliocene and upper or middle Miocene.	Malumbang series	Upper limestone. Coralline to sandy. Cudiapi sandstone. Bedded, calcareous, yellow to brown in color.	20–50 50–100	*Trochus fenestratus, Cerithium nodulosum, Telescopium* sp., *Conus flavidus.*	Shallow seas, clear at times.
		Lower limestone, white to yellow. coralline in part.	* 0–20	*Pyrula gigas, Lucina bacauensis, Cerithium* sp., *Solecurtus grandis* sp. nov., *Spondylus imperialis, Operculina costata, Bulla ampulla, Pecten senatorius, Lithothamnium ramosissimum.*	
Middle or lower Miocene.	Canguinsa sandstone.	Blue to gray, massive, clayey sandstone with gray calcareous sandstone and minor beds of limestone locally. A single small outcrop of volcanic agglomerate in base, not of general occurrence.	50–160	Large lepidocyclinas, *Cycloclypeus communis.*	Nonuniform conditions; both deep or quiet and shallow seas indicated; local extrusion.
Unconformity. Mechanical discordance and possible erosion.					

Lower Miocene or Oligocene. (?)	Vigo shale	Sandstone and fine sandy conglomerate, in alternate beds.	(?)	*Mitra* sp., *Pyrula* sp
		Bacau stage. Massive or imperfectly bedded, bluish black shale with minor sandy zones. The principal oil seeps are associated with the Bacau stage and shallow wells have obtained fair showings of oil in it. A single outcrop of volcanic agglomerate at this horizon, but not of general occurrence.	50–100	*Conus loroisii, Conus striatellus, Globigerina, Conus hochstetteri, Tapes rimosa.*	Local extrusion. Shallow seas, gradual subsidence. Water deepened late in the period but became very shallow at close.
		Gray shale, black shale, yellow and brown sandy shale, and sandstone interbedded in thin layers. Traces of oil and gas. Possible oil horizon in unexposed base. A single small exposure of volcanic agglomerate; not of general occurrence.	ª1,400;	*Globigerina, Polystomella*	
Eocene		Concealed or lacking			
Unconformity					
(?)		Basal conglomerate over diorite			

ª Base not exposed.

TABLE II.—*Stratigraphy of the Echigo oil field, Echigo, Japan, according to T. Iki.*

Series.	Character.	Thickness.
		Meters.
Recent -------------------------	Alluvium; clay, sand, and gravel-------------------	-----------
Pleistocene---------------------	Diluvium; ancient river terraces -------------------	-----------
Pleistocene or Pliocene-----------	Unconsolidated clay, sand, and gravel -------------	-----------
Pliocene ------------------------	Clayey shale, sandstone and conglomerate, and lignite beds.	-----------
Miocene -----------------------	Gray sandy shale and subordinate layers of sandstone in which oil exists. A bed of fossiliferous limestone in this stage contains *Lithothamnium ramosissimum* Reuss. Shale is locally petroliferous. Interbedded andesitic agglomerate.	300–600
	Black hard shale grading upward into gray sandstone. Interbedded andesitic agglomerate.	600
Miocene? (Lowest beds Eocene?) --	Black shale with thin beds of bluish sandstone and thick beds of white or bluish tuff sandstone which is oil bearing.	1,800 +

TABLE III.—*Stratigraphy of the Moera Enim oil field in southern Sumatra according to Aug. Tobler.*

Series.	Character.	Thickness.
		Meters.
Recent and younger Pleistocene.	River alluvium, most recent tuff deposits, terraces, etc.	----------
Older Pleistocene---------------	Tuff and agglomerate, older terraces, etc. Effusive rocks locally.	----------
Unconformity -----------------		----------
Pliocene (?)--------------------	Upper Palembang formation. Tuff, sandstone, and conglomerate. Fresh-water forms in the lower, well-bedded part, silicified wood. Sub-aërial and lacrustine origin. Effusive rocks locally.	830
	Middle Palembang formation. Marl and marly sandstones. Bedded sandstones and unbedded clays with lignite beds. Estuary formation. Important oil horizon.	650
Miocene { Middle-----	Lower Palembang formation. Shale and fine-grained sandstone. Marine fossils. Volcanic material, marl, and local coral reefs. Important oil horizon.	1,100+
{ Lower-----	Shale with interbedded limestone and calcareous sandstone. Locally, clastic sediments, conglomerate, tuff, agglomerate, sandstone, and marl. Marine formation. Doubtful oil horizon.	
Unconformity -----------------	Andesitic effusive rocks-----------------------	----------
Oligocene----------------------	Stage IV. Orbitoidal limestone------------------	----------
	Stage III. Bedded marl and fossiliferous limestone. Petroleum bearing?	
	Marl with leaf impressions and fossil fish scales ---	----------
Eocene -----------------------	Stage II. Clay, shale, and thin beds of coal--------	----------
	Stage I. Breccia and conglomerate. Coal bearing-	----------
Gneiss and schist with granite and diorite intrusions.		----------

General geologic sections.—An adequate description of the individual stages is made difficult by the irregularity and variability of the upper strata. The limestones and calcareous sandstone of the Malumbang series are especially troublesome in this respect and cannot be sharply defined. In reality all the strata above the Vigo shale might be described as one formation— massive sandy clay at the base, grading upward into sandstone and limestone. Thus defined, the formation has a thickness of about 250 meters.

As a preface to the discussion of the separate formations, general geologic sections obtained in different parts of the region will be recorded. It should be remembered that the thicknesses assigned to the various formations are estimates only, and are not based upon accurate data.

In the latitude of Matataha and Vigo Rivers a thickness of the Vigo shale greater than is exposed elsewhere is encountered in the limbs of the Central anticline near the middle of the peninsula. Toward the coasts on either side the upper formations appear overlying the Vigo shale. The section through the rocks east of the anticlinal axis is shown in Table IV.

TABLE IV.—*Geologic section from the seacoast westward through Cambagaco Ridge and Vigo Valley to the axis of the Central anticline.*

Formation.	Description.	Approximate thickness.
		Meters.
Recent	Raised coral reefs and alluvium. Coastal plain	10
Unconformity		
Malumbang series	Upper limestone. Coralline; eastern slope of Cambagaco Ridge; thick bedded to massive; dip 30° northeast.	30
	Cudiapi sandstone. Bedded, yellow to brown sandstone; calcareous and of medium-grain size; local crossbedding; summit of Mount Cambagaco.	40
	Lower limestone; gray to white; thick bedded or massive; locally concretionary; dip 45° northeast.	20
Canguinsa sandstone	Gray clayey sandstone, usually bedded; west slope of Cambagaco Ridge.	70
	Sandy massive clay; blue to gray in color: close jointed in some exposures; dip 30° to 40° (north of Vigo River to northeast, south of Vigo River to southeast); abundant fossils in parts of base; a single outcrop of volcanic agglomerate interbedded (?) in base on Vigo River at the mouth of Bagacay Creek.	80
Unconformity	Abrupt increase in the angle of dip; western base of Cambagaco Ridge.	
Vigo shale	Bacau stage. Grayish blue to black shale; fine grained and bedded; dip 60° to 80° east-north-east; traces of oil and inflammable gas. Volcanic agglomerate and massive andesite (flow?), a single outcrop on Tangob Creek; included in shale.	100
	Shale interbedded with sandy shale and occasional layers of sandstone, all thin bedded; strikes in various directions, dips usually steep; nearer axis of anticline, dips become uniform 55° to 65° east-northeast. Vertical in axis; base not exposed. Regular strata east of the anticlinal axis probably at least 800 meters thick.	

On Dumalog Creek (Table XIII) north of the line of the section in Table IV, sandstone and conglomeratic sandstone occur above the Bacau stage of the Vigo shale apparently bedded in conformity with the shale below them, and a small outcrop of volcanic agglomerate is found at an apparently lower horizon in the Vigo shale than that of the agglomerate on Tangob Creek.

The Vigo shale appears to undergo a change in character from east to west in that the upper beds become more sandy. This lateral transition from shale to sandstone is revealed by comparing Table V, which is a section of the western limb of the Central anticline, exposed in Matataha River, with Table IV. The Canguinsa sandstone is not well exposed along the western coast, and cannot be separated sharply from the Vigo shale. The evidence of unconformity at the base of the Canguinsa sandstone which was noted in Table IV does not appear in the Matataha River section.

TABLE V.—*Geologic section along Matataha River from the western coast to the axis of the Central anticline.*

Formation.	Description.	Approximate thickness.
		Meters.
Malumbang series_____	Lower limestone, yellow to white coralline limestone overlying sandy, bedded limestone; dip 35° southwest.	30
Canguinsa sandstone_____	Concealed interval _____	50
Canguinsa sandstone, Vigo shale _____	Interbedded sandstone, sandy shale, and shale with occasional conglomeratic sandstone beds with small pebbles of diorite, andesite, etc.; gray to brown or yellow; almost horizontal in Mount Cancalao.	250
Vigo shale_____	Blue to black shale (Bacau stage?); traces of inflammable gas; base of Mount Cancalao.	20
	Sandstone and shale interbedded, dip southwest, increasing toward the east up to 25°.	800
	Thin-bedded shale, sandy shale, and sandstone, general color brown or yellow; dip west-southwest increasing toward the east from 25° to 70°; strata vertical in axis of anticline.	500

The upper formations are exposed in section along the crest of the Central anticline in the valley of upper Canguinsa River while the Vigo shale is uncovered in scattered outcrops only. The section in Table VI was obtained in Balinsog Hill and the eastern wall of the valley of Canguinsa River. Table VII shows

the relations in the opposite (western) limb of the anticline observed in the western slope of South Cudiapi Mountain and the western wall of Canguinsa River valley along Amuntay Creek. Table VIII is a section in the eastern limb at Bacau.

TABLE VI.—*Geologic section from the summit of Balinsog Hill downward to the bed of Canguinsa River.*

Formation.	Description.	Approximate thickness.
		Meters.
Malumbang series _____	Upper limestone. Coralline, massive, yellow to white limestone; not present except in remnants on Balinsog Hill, but found on neighboring hills.	20
	Cudiapi sandstone. Bedded, brown to yellow, calcareous sandstone; alternate beds of different thicknesses; dip 15° eastward.	100
	Lower limestone? Concealed or lacking _____	_____
Canguinsa sandstone _____	Gray calcareous sandstone; bedded, dip slight to eastward.	100
	Gray medium-grained sandstone with abundant sandstone concretions.	10
	Gray sandy clay, massive; fossiliferous _____	20
Unconformity? _____		_____
Vigo shale _____	Bacau stage. Blue to black thin-bedded shale; occasional outcrops only.	_____

TABLE VII.—*Geologic section down the east slope of South Cudiapi Mountain along Amuntay Creek to upper Canguinsa River.*

Formation.	Description.	Approximate thickness.
		Meters.
Malumbang series _____	Upper limestone? Not present; removed by erosion?	_____
	Cudiapi sandstone. Yellow to brown calcareous sandstone, bedded; medium-grain size; summit of South Cudiapi Mountain.	80
	Lower limestone. Yellow to white coralline limestone exposed at base of peak of South Cudiapi Mountain.	20
Canguinsa sandstone _____	Imperfectly bedded, gray to yellow calcareous sandstone; dip to westward.	60
	Gray to light blue sandy clay; compact and jointed; not bedded; fossiliferous.	100
Unconformity? _____		_____
Vigo shale _____	Bacau stage. Occasional outcrops only, along Canguinsa River; blue to black, thin-bedded shale; dips steep to east and west.	_____

TABLE VIII.—*Geologic section in the eastern wall of Canguinsa Valley at Bacau; from the rim of the valley to the bed of the river.*

Formation.	Description.	Approximate thickness.
		Meters.
Malumbang series	Upper limestone; yellow to white coralline and sandy limestone, imperfectly bedded; dip 15° to 25° northeast.	30
	Cudiapi sandstone; calcareous, medium-grained sandstone; alternate beds of different thicknesses; dip 15° to 45° northeast.	80
	Lower limestone; coralline; poor exposures, not certainly in place.	20
Canguinsa sandstone	Gray sandstone, jointed and clayey; exposures poor	100
Unconformity; abrupt change in angle of dip.		
Vigo shale	Bacau stage; blue to black petroliferous shale, petroleum seep; bedding is indistinct and appearance massive; fine-grained clay shale with irregular, subordinate sandy zones; dip 55° east-northeast.	30
	Thin-bedded blue to black shale; occasional layers of sandstone; dip 60° east-northeast; outcrops in stream floor.	

Above the Vigo shale in the western wall of Canguinsa Valley at Bacau there are about 100 meters of clayey gray sandstone. About 1 kilometer farther to the northwest the Lower limestone occurs above this sandstone.

The section in Table IX represents the eastern face of South Cudiapi Mountain down to Cauayan Creek. The rocks here dip eastward at low angles, lying in the western limb of the Ayoni anticline.

TABLE IX.—*Geologic section down the western slope of South Cudiapi Mountain to Cauayan Creek.*

Formation.	Description.	Approximate thickness.
		Meters.
Malumbang series	Upper limestone; not present; removed by erosion?	
	Cudiapi sandstone; yellow to brown calcareous sandstone; bedded, medium-grain size; summit of South Cudiapi Mountain.	80
	Lower limestone; yellow to white coralline limestone.	20
Canguinsa sandstone	Gray clayey sandstone; bedded and calcareous in upper portion; massive, sandy fossiliferous clay at base.	170
Unconformity		
Vigo shale	Bacau stage; blue to black thin-bedded shale, traces of inflammable gas; occasional exposures only.	

The lower part of Bahay River, where it cuts through the eastern limb of the Maglihi anticline to the eastern coast, exposes the section recorded in Table X.

TABLE X.—*Geologic section on the lower part of Bahay River; from the mouth of the river inland.*

Formation.	Description.	Approximate thickness.
		Meters.
Recent _____	Yellow to brown raised coral reefs and coral sand; coastal plain.	10
Unconformity _____		
Malumbang series_____	Upper limestone; coralline; dip 30° northeast; east slope of the ridge near coast.	15
	Cudiapi sandstone? __}concealed interval _____ Lower limestone?____}	100
Canguinsa sandstone_____	Gray, bedded, clayey sandstone; dip 35° northeast.	140
Canguinsa sandstone? _____	Gravel or conglomerate, sandy matrix, large pebbles of diorite, quartz, crystalline orbitoidal limestone, etc.	5
	Coralline limestone grading into calcareous sandstone at base; dip 45° northeast.	8
Unconformity? _____		
Vigo shale? _____	Sandstone and shale, irregular thin beds; small seams of lignite; dip 55° northeast.	10
	Sandy blue clay _____	3
Vigo shale_____	Brown coarse-grained sandstone, thick bedded to massive; carbonized leaf impressions.	10
	Blue to black carbonaceous shale; sandy; base not exposed; dip 55° northeast; occasional outcrops only; 1,500 meters northwest of the line of this section at about this horizon oil seeps from Bacau stage of Vigo shale on Milipilijuan Creek and at a somewhat greater distance southeast at Bahay, oil seeps from a concealed formation.	

The gravel and coralline limestone between the Vigo shale proper and the Canguinsa sandstone in the foregoing section are unusual and their correlation is doubtful. It should be stated that the character of the gravel and the relations of its occurrence allay any suspicion that it is a recent, superimposed deposit.

Near Mount Morabi in the eastern limb of the Maglihi anticline, south of Bahay, the section shown in Table XI was obtained.

TABLE XI.—*Geologic section in the vicinity of Mount Morabi; from the coast at San Andres to the summit of the mountain.*

Formation.	Description.	Approximate thickness.
		Meters.
Recent	Yellow to brown, coralline, sandy limestone, lies nearly horizontal; narrow coastal plain, vicinity of San Andres.	10
	Upper limestone, coralline	15
Malumbang series........	Cudiapi sandstone. Bedded calcareous sandstone. Dip 30° east.	30
	Lower limestone, coralline to sandy................	30
	Bedded, gray, calcareous sandstone; dip 55° east: east face of Mount Maglihi and Mount Morabi.	50
Canguinsa sandstone............	Yellow to white limestone with abundant coarse sand, locally small pebbles of diorite and quartz, large lepidocyclinas; dips steeply to east, vertical and even overturned to west; summits of Mount Maglihi and Mount Morabi.	5
	Gray calcareous sandstone, bedded; west face of Mount Maglihi.	20
	Clayey, massive sandstone; valley west of Mount Maglihi.	40
Unconformity?		
Vigo shale..................	Bacau stage; bedded blue to gray shale with sandstone. Occasional outcrops in Canibo Creek; steep dips to east and west, thickness of a few meters only exposed; oil seep at Banco; salt water in Maalat Creek.	

A final section obtained at the village of Cubcub (outside the area mapped), about 15 kilometers northwest of San Narciso, is shown in Table XII.

TABLE XII.—*Geologic section on Guinhalinan River in the vicinity of Cubcub, Peris.*

Formation.	Description.	Approximate thickness.
		Meters.
Malumbang series_____	Upper limestone; coralline; isolated patches only; summit of Mount Bogas.	10
	Cudiapi sandstone; bedded, calcareous, fossiliferous; toward base, clayey.	80
	Lower limestone? Concealed or lacking _____	_____
Canguinsa sandstone_____	Gray, sandy clay, massive and fossiliferous. Tinaplaca Creek.	100
	Brown coarse-grained sandstone; traces of inflammable gas. Tinalpaca Creek.	8
Vigo shale_____	Thin-bedded shale with occasional sandstone beds; Tinaplaca Creek, Pigsaan Creek and Guinhalinan River at Cubcub. Extensive exposure at Cubcub; in upper part, sandstone beds 10 centimeters to 1 meter thick with blue to gray, fine-grained, thin-bedded shale and brown, sandy shale; farther down in series fewer sandstone beds, more sandy shale in thin beds alternating with shale of finer grain. Strata lie inclined at an angle of 30° and show subordinate buckling in lower part of series; thickness in continuous exposure, 250 meters; indicated additional thickness, 350 meters; base not exposed.	600+

Alluvium and travertine.—Recent alluvium is found along the valleys of Pagsanhan, Vigo, Mulanay, and Ayoni Rivers. It occurs near the mouth of the Pagsanhan, but on the other rivers it is most extensive along the middle courses above the gaps through which these rivers enter the sea. The material consists of clay and sand with subordinate quantities of sandstone and limestone gravel. Fresh-water shells and occasionally pieces of wood partly carbonized are found in the alluvium. The river terraces usually rise less than 6 meters above the level of the stream.

Travertine is also deposited by running water throughout Bondoc Peninsula and is of more general distribution than alluvium, although as a geologic formation it is subordinate. The salts of calcium which are deposited as travertine are leached from the limestone and calcareous sandstone strata, usually by surface waters. Deposits from springs are exceptional. As is

usual with travertine deposited by streams, the formation is most extensive over faces of waterfalls where beautiful rounded terraces often develop; but wherever the streams flow rapidly enough to break into ripples, travertine is precipitated abundantly, and even in still water a veneer of travertine covers the whole stream floor.

Where the flow is rapid, the travertine is eventually built up so as to raise the stream level. As soon as the travertine forms a barrier in this way it accelerates its own growth and ultimately becomes a natural dam. Stream ponding is thus developed, or the water may be diverted to a new channel adjacent to the old bed. A curious interpretation of this phenomenon has grown up among some of the prospectors familiar with the Tayabas field. As it is commonly expressed: "Where a river dams itself up, you are close to oil." A possible slight basis for this belief may be found in the fact that the petroliferous or carbonaceous beds precipitate the calcareous salts from the water, and are usually coated with travertine in consequence. However, since decomposing vegetable matter, such as fallen leaves and twigs, and evaporation from the surface of the water are active precipitating agents, this rule of thumb method of prospecting leaves much to be desired. On the other hand, the travertine seriously retards geologic study in that it often conceals the formations along the streams where they would otherwise be open to examination.

Littoral deposits and recent coral reefs.—Narrow coastal plains, composed mainly of raised coral reefs, occur at intervals, bordering the peninsula. Clay, sand, and other shore materials are intermingled with the corals in varying degrees. The result is a yellow to white, heterogeneous, unconsolidated formation without distinct or regular bedding planes, which is generally youthful in aspect. Shells and fragments of coral closely related to species that are to be found alive in the adjacent seas are prominent constituents of the rock. The disintegration product is a brownish yellow sandy clay which generally covers the ground surface.

These deposits lie nearly horizontal and are found from sea level to an elevation of at least 15 meters. The coastal plain between the mouth of Ajus River and Catanauan attains a greater elevation than 15 meters, but here, as well as elsewhere, it is difficult to delimit the raised reefs from the older coralline limestone. Numerous small areas of mangrove-covered littoral deposits are to be seen farther south along this coast. On the

west coast, the formation is to be found in the region of Minajero Bay and north beyond San Andres. Between the mouths of Bahay and Vigo Rivers and farther north near San Narciso, the vicinity of the coast line is made up of littoral deposits.

At various places over the surface of the littoral formation shells were observed which probably represent the molluscan fauna existing when the benches were below sea level. All the species identified are still living, and many of them are edible. Numerous deserted kitchen middens are encountered near the coast, and it is possible that some of the shells collected came from these middens and do not represent the formation upon which they were found.

The genera and species noted are as follows (Plate I) :

Spondylus.	*Potamides* sp.
Conus flavidus Lamarck.	*Voluta* sp.
Trochus fenestratus Gmel.	*Natica* sp.
Arca cecillei Phil. (?)	*Crista pectinata* Linn.
Astralium stellare Gmel.	*Strombus canarium* Linn.
Cerithium nodulosum Brug.	*Telescopium telescopium* Linn.
Cerithium jenkinsi K. Mart. (?)	

Malumbang series.—The Malumbang series at the top of the column of folded strata consists of the Cudiapi sandstone, which is generally, but not invariably, included between limestones. The limestones are sandy and at many places are either missing or cannot be distinguished from the sandstone which is usually calcareous. They are brownish yellow to white, and generally massive or in thick poorly defined beds. Locally, and usually in the sandy facies, the limestone is bedded, the individual layers averaging from 15 to 30 centimeters thick.

The Upper limestone is generally coralline, although the transition between it and the calcareous sandstone below is gradual. At places on the coast where it is not highly inclined, it cannot be delimited from the recently raised reefs. In representative exposures it shows a thickness of about 30 meters.

The Cudiapi sandstone is named from a type occurrence in the summit of South Cudiapi Mountain. In many places it exhibits alternate beds of different thicknesses; the thinner beds are more calcareous and harder than the intervening thicker beds, and are more resistant to weathering so that the outcrops are characterized by the protruding edges of the thin beds. Where the Lower limestone is missing, the Cudiapi sandstone cannot be separated sharply from the underlying Canguinsa sandstone. The estimated thickness of the Cudiapi sandstone

ranges from 40 to 135 meters.   The exposure on the summit of South Cudiapi Mountain is about 80 meters thick.

The Lower limestone is generally less than 20 meters thick. It is harder and more compact than the Upper limestone, and is more frequently bedded.   In other respects, the limestones of the two horizons are similar and hardly to be distinguished.

On Mount Cambagaco, in the stratigraphic position of the Lower limestone, a rock of unusual appearance is to be seen. It is composed mainly of limestone concretions, 1 centimeter or more in diameter, which have a concentric structure.   The concretions lie close together in a cement which is also calcareous, giving the rocks a magnified oölitic texture.   This particular variety of the Lower limestone was not observed outside the one vicinity near Mount Cambagaco.

The Malumbang series attains its greatest development in the vicinity of Malumbang Plain extending north beyond Balinsog Hill, south through Mount Banaba and Mount Guinamuan, and southwest to Tala and Sili with a detached area farther south on top of Bondoc Head (see geologic map).   The lower two members are found in the Cudiapi Range, while the ridge along the east coast consists of a single limestone (Lower?) overlying the Vigo shale with a concealed interval between.   San Narciso Peninsula is covered by the Upper limestone.

All three horizons in the Malumbang series are fossiliferous. Fossils were collected at two places on the hills at the northern edge of Malumbang Plain, which are capped by the Upper limestone.   Specimens from fossil locality 61 were obtained on the hills north of Mount Anuing near the eastern rim of Canguinsa River valley at Bacau, and others (fossil locality 63) were found on the hills immediately to the east on the northern border on Malumbang Plain.   The Upper limestone in this vicinity is sandy, and grades imperceptibly into the Cudiapi sandstone below it.   The fossils are embedded in sandy, calcareous material which might be designated either as sandstone or limestone.

Fossils collected at locality 61.

Pecten senatorius Gmel. +	*Conus* indet.
Pecten leopardus (?) Reeve. +	*Olivia* indet.
Cytherea indet.	*Strombus labiosus* Gray. +
Cardium indet.	*Melania* sp.
Schizaster subrhomboidalis Herkl.	*Dosinia* sp.
Xenophora dunkeri K. Mart. (?)	*Lagenum multiforme* K. Mart. var.
Turbo indet.	tayabum var. nov.

Fossils collected at locality 63.

Conus indet.

Pecten senatorius Gmel. +

Mitra indet.

Xenophora indet.

Spondylus imperialis Chem. +

Operculina costata d'Orb. +

Turbo borneënsis (?) Bttg.

Trochus sp.

Bulla ampulla Linn. +

Oliva indet.

Pattalophyllia sp. +

Cycloseries sp.

Of the determinable fossils in these and the following lists, those which represent living species are indicated by a plus sign.

Fossils were obtained from the Cudiapi sandstone at three different places, as follows: (1) Fossil locality 65, calcareous sandstone immediately beneath the Upper limestone in the hills north of Malumbang Plain, adjacent to fossil locality 61; (2) fossil locality 4, calcareous sandstone beneath the Upper lime-stone about 450 meters south of Balinsog Hill, at an elevation of 360 meters; (3) fossil locality 13, sandstone, at an elevation of 270 meters on the high ground between Apad and Milipilijuan Creeks, affluents of the Bahay River. The Upper limestone does not occur over the sandstone at this place, but the sandstone itself is very calcareous.

The fossils from the Cudiapi sandstone were determined as follows:

From fossil locality 65.

Pecten sp.

Schizaster subrhomboidalis Herkl.

Dosinia sp.

From fossil locality 4.

Turbo sp. indet.

Nassa sp. indet.

Fusus sp. indet.

Pleurotoma sp. indet.

Melania sp. indet.

From fossil locality 13.

Clementia sp. indet.

Xenophora dunkeri K. Mart.

Ostrea orientalis Chem. (?) +

Pecten senatorius Gmel. +

Cerithium herklotsi K. Mart.

Pleurotoma tjemoroënsis K. Mart.

Pleurotoma carinata Gray. +

Fossils from limestone at a horizon corresponding stratigraph-ically with that of the Lower limestone were collected at three localities, namely: Fossil locality 44, at the mouth of Ayoni River; fossil locality 59, on a prominent hill (elevation, 250 meters) 2 kilometers west of Tala; and fossil locality 25, near Tambo, a barrio of San Narciso. However, as will appear in the dis-cussion of the field relations at these localities, only the last group in the foregoing list represents certainly the Lower limestone; the fossils from the other localities may belong to either the Upper or Lower limestone.

On the north side of Ayoni River near its mouth, fossils were

found in the limestone which forms the ridge along the western coast of the peninsula.

Fossils collected at locality 44.

Cypraea sp. indet.
Arca nodosa K. Mart. (?)
Schizaster sp.

Cerithium sp. indet.; large internal cast.

Along the western coast from Ayoni north to Catanauan, this limestone is found in the coastal ridge, and occurs conformably only a short distance above beds which clearly belong to the Vigo shale. A short distance inland from Ayoni similar limestone occurs above the Canguinsa sandstone, and is overlain at places by the Cudiapi sandstone. This relation suggests that the limestone at Ayoni is the Lower limestone, but the evidence is not conclusive and either limestone horizon may be represented by the fossils from this locality.

Fossils collected at locality 59.

Pyrula gigas K. Mart.
Balanus sp.

Pecten leopardus K. Mart.

The limestone in which these fossils were found occurs on the top of a hill; below the limestone, with a concealed interval between, the Canguinsa sandstone was observed. The thickness of the concealed beds is hardly great enough to include the Cudiapi sandstone and the Lower limestone in their usual thicknesses. The fossils, therefore, are assigned to the Lower limestone, although they may represent the Upper limestone instead.

A sample of limestone (fossil locality 25), which certainly came from the Lower limestone horizon, was collected near the Cabongahan-San Narciso trail at an elevation of 180 meters, on the east side of the ridge extending northwest from Mount Cambagaco. Thin sections of this rock show small fragments of limestone and the well-known alga, *Lithothamnium ramosissimum* Reuss, intermingled in a cement of calcite.

Plates II and III are photographs of typical fossils from the Malumbang series. Plate II represents the Upper limestone and the Cudiapi sandstone, while Plate III shows fossils from the Lower (?) limestone.

The most conclusive evidence as to the age of the Malumbang series is found in the Lower limestone, which, on the basis of the fossil *Lithothamnium ramosissimum* Reuss (fossil locality 25) may be assigned to the Miocene. The upper beds in the series are apparently as young as the upper Miocene or the Pliocene. The formation is similar to the "étage marneux" which Ver-

beek[12] assigns to the middle stage of the upper Tertiary for Java, and describes as follows:

IX. Middle stage of the upper Tertiary. ⎫
     Formations called the marl stage.   ⎪ Middle and upper Miocene
     Abundant marl and marly sandstones. ⎬   highest beds in part Plio-
     Less abundant sandstone and shale with⎪ cene.
     some calcareous beds.   ⎭

     * * * IX The second stage or the middle Neo-Tertiary stage m₂, probably contains at a slightly lesser depth than the lower division, some beds of Middle and Neo-Miocene and even Pliocene age, which cannot always be distinguished in the field and are called by us the "marl stage" on account of the principal rock. One finds here, besides some calcareous sandstones with numerous marine shells, beds of conglomerates and breccias (much less than in the stage M), then some shales, noncalcareous sandstones and calcareous beds, the last named having occasionally orbitoides with spatula shaped chambers (lepidocyclines) * * *.

The Cudiapi sandstone, the principal rock in the Malumbang series, might be called a marly sandstone, and the limestones are likewise often sandy or clayey. Shale is not present, but some exposures of the Cudiapi sandstone are argillaceous.

No indications of petroleum have been observed in the Malumbang series. It is above the horizon at which oil seeps occur, and bears on the possible petroleum industry only in the fact that it must be drilled through before the petroliferous zones can be explored in parts of the promising territory.

Canguinsa sandstone.—The Canguinsa sandstone is a close-grained, gray or blue rock to which the term sandstone applies in a general way. It is distinguished from the Cudiapi sandstone by its massive or less perfectly bedded appearance and by the considerable proportion of clay which characterizes it. The upper portion is usually a soft, clayey sandstone, imperfectly bedded and occasionally close jointed. This sandstone is calcareous, and several exposures on the upper part of the Canguinsa River are concretionary. The concretions are aligned so as to lend a bedded appearance to the exposure. The concretionary sandstone was not observed to be of general distribution.

Toward the base of the formation either a typical sandstone or an indurated massive or jointed clay is encountered. Both sandstone and clay occur in heavy banks from 3 to 6 meters thick, and both are slightly calcareous. The sandstone facies in the basal portion is deep blue on fresh exposure, but weathered surfaces are gray or brown. Ordinarily, it is of medium-grain size, and shows little evidence of bedding. The clay is also blue

[12] Verbeek and Fennema, Description Géologique de Java et Madoura. Amsterdam (1896), 1, 38, 41.

when freshly exposed, and becomes gray upon weathering; it is fine and compact, but not bedded.   Some of the rocks which have been classed as marl in Java and Sumatra are probably similar to the slightly calcareous clayey zone in the Canguinsa sandstone.

The clay and sandstone banks in the base of the formation are fossiliferous and sometimes contain myriads of small shells.   The fossils are often greasy and appear to be well preserved, but in reality they are very fragile, and can be removed entire only with care.

In the section on lower Bahay River, the Canguinsa sandstone includes a few meters of limestone and conglomerate.   On Mount Maglihi and Mount Morabi limestone which contains coarse sand and small pebbles of diorite, quartz, and andesite is present in the Canguinsa sandstone, but no conglomerate was observed. In the lower part of the gorge on Canguinsa River, also, a subordinate thickness of limestone was found in the Canguinsa sandstone.

Volcanic agglomerate, with some appearance of bedding, outcrops at the junction of Bagacay Creek and Vigo River in the base of the Canguinsa sandstone, or possibly between it and the underlying formation.   The outcrop is of limited extent, and is the only instance of volcanic rocks above the Vigo shale.

The thickness of the Canguinsa sandstone varies from 50 to 160 meters.   Although it occurs unconformably over the Vigo shale, the contact between the two formations is found always near the same horizon in the Vigo shale, and the base of the Canguinsa sandstone serves as a datum for rough correlation.

The Canguinsa sandstone is not encountered in large areas, but occurs in steep slopes along streams where it has been protected from erosion by the overlying Malumbang series.   It is exposed at the surface or overlain by patches of the Lower limestone, in parts of Malipa Creek valley, and is prominent among the rocks of the Cambagaco-Dagmit ridge along the eastern coast.   On the western coast it is little in evidence, although it occurs in the western slope of South Cudiapi Mountain.   Calcareous sandstone and limestone, overlying Vigo shale and consequently referred to the Canguinsa formation, cap a ridge between two branches af Mulanay River in the northern part of the field. Pieces of agglomerate, in which, among other constituents, pebbles of schist were noted, are found in this vicinity, and are probably to be referred to the volcanic agglomerate horizon.

Two groups of fossils from the Canguinsa sandstone proper (fossil localities 7 and 12) ; and fossils from the included limestone beds on Mount Morabi (fossil locality 62) and Mount Mag-

lihi (fossil locality 67) have been studied; photographs of some of the specimens appear on Plate IV.

Fossils were found in the Canguinsa sandstone on Amuntay Creek (affluent of Canguinsa River) at an elevation of 150 meters. Here the Canguinsa sandstone is about 160 meters thick (see geological section, Table VII). The fossils were found about 40 meters above the base of the formation in tough jointed gray clay. They include:

Fossils collected at locality 7.

Pecten fricatum Rv. +	*Dosinia* sp. indet.
Pecten sp.	*Pleurotoma suturalis* Gray (?) +
Pecten senatorius Gmel. +	

The following fossils were collected from a clayey, blue sandstone in the base of the Canguinsa immediately above the Vigo shale on the upper part of Tangob Creek, about 50 meters northeast of the main occurrence of volcanic agglomerate shown on the geologic map.

Fossils collected at locality 12.

Strombus canarium Linn.	*Pattalophyllia* sp.
Conus ornatissimus K. Mart.	*Septarea arenaria* Lam. +
Corbula socialis K. Mart.	*Mitra javana* K. Mart.
Cypraea erosa Linn. +	*Natica mamilla* Linn. +
Hindsia sp.	*Ranella* sp.
Pleurotoma flavidula Lam.	

A microscopic section through a specimen of the limestone occurring in the Canguinsa sandstone on Mount Maglihi (fossil locality 67) showed it to be made up of fragments of sandstone, quartz, and limestone in a calcareous cement and to contain Foraminifera with lozenge-shaped cells, probably of the genus *Lepidocyclina*. The limestone from Mount Morabi (fossil locality 62) contains *Cycloclypeus communis* K. Martin, which represents the middle Miocene, and large lepidocyclinas some of which are 45 millimeters in diameter and 5 millimeters broad in the thickened central portion. *Lepidocyclina richthofeni* Smith was identified among these. This species has been referred by Douvillé [13] to the lower Miocene.

No definite age determinations can be made from the fossils in the Canguinsa sandstone proper. The fossils in the included limestone, however, are well known and have been used in correlation by various authorities. From their presence it is concluded that the Canguinsa sandstone should be placed in the middle Miocene, extending, perhaps, into the lower Miocene.

The Canguinsa sandstone occurs immediately above the prin-

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[13] *Compt. rend. Soc. géol. de France* (1909), 14, 130.

cipal known oil horizon. It is not porous enough to afford a reservoir in which oil might accumulate, and no oil has been observed in it. Because of its compact nature on the other hand, it would tend to confine any oil collecting below it. At several promising drilling sites the Canguinsa sandstone must be drilled through before the petroleum zone is encountered.

Vigo shale.—The base of the Canguinsa sandstone is marked by an unconformity, which is partly of a mechanical nature, but may represent also a period during which the underlying formation, the Vigo shale, was subjected to erosion. The subject of unconformities is discussed in connection with the geologic structure, page 337.

The Vigo shale is the most extensive and the most uniform series in the stratigraphic column of Bondoc Peninsula. The beds belonging to this formation, although they are closely related in type to some of the overlying beds, constitute a separate stratigraphic division which is readily distinguished.

The type exposures in the valley of Vigo River consist of fine-grained shale and sandy shale interstratified in thin regular beds from 5 to 10 centimeters in thickness. Occasional beds of sandstone occur varying from 10 centimeters to 1 meter in thickness. The fine-grained shale is gray, blue, or black, and is made up almost entirely of clay. The sandstone is gray or brown, and consists of uniform, medium-sized, not completely rounded grains of quartz, diorite, andesite, and metamorphic rocks. The sandy shale is yellow or brown and of intermediate composition.

There is an apparent transition from east to west in the character of the Vigo shale. In the eastern limb of the Central anticline, exposed in the valley of Vigo River, the formation is predominately shale throughout, sandstone occurring only at intervals. In the western limb shale predominates in the exposure near the axis only, that is, the lower part of the series. Farther to the west the sandstone beds increase in number, until in the upper horizons they become more prominent than the shale. The grain-size likewise increases in the upper beds, and small pebbles occur, forming layers of sandy conglomerate.

The blue or black, fine-grained shale in the Vigo formation usually emits a slight odor of light oils upon fresh fracture, and in some outcrops is highly petroliferous. The material loses this odor and assumes a light gray color after it has been exposed to the air and has become thoroughly dry. The petroliferous shale forms a loosely defined stage in the upper part of the Vigo, which will be referred to as the Bacau stage, although it cannot be sharply delimited.

The Bacau stage contains fewer beds of sandstone than the Vigo shale proper, and the bedding planes are often less distinct; thus, exposures at Bacau and Sili have the appearance of massive banks of compact, hardened clay, which are sandy in subordinate, irregular zones only. To material of this character the ordinary definition of shale which stipulates a fissile or laminated texture does not apply strictly, but the term is convenient and, employed in a broad sense, is preferable to "clay" or "clay-shale" in describing the rocks in the Bacau stage. The shale weathers into concretion-like ellipsoidal pieces from which concentric layers split off, and break into small fragments with conchoidal surfaces. The manner of weathering distinguishes the petroliferous beds from other fine-grained layers in the Vigo which are fissile and split into flakes upon disintegration.

Beds analogous in character to those in the Bacau stage are found throughout the Vigo shale, but the Bacau stage proper appears to be confined to a zone from 50 to 75 meters thick in the upper portion. In the eastern half of the field, the Canguinsa sandstone overlies the Bacau stage in a majority of exposures. Occasionally (section on Dumalog Creek, Table XIII, page 333; and on Bahay River, Table X, page 320), sandstone and fine conglomerate, which are evidently a part of the Vigo series, occur above the Bacau stage. In the western part of the peninsula sandy conglomerate is found near the top of the Vigo formation. These overlying beds may be always present above the Bacau stage, but concealed generally by an overlap of the unconformable Canguinsa sandstone. The sandstone and conglomerate in the upper part of the Vigo shale are generally micaceous, and show many carbonized leaf-impressions. In the southwestern part of the field, large pieces of silicified wood were observed in the conglomerate, and on Bunsaua Creek a bed of lignite 20 centimeters thick occurs in the shale below this horizon.

Two exposures of andesitic agglomerate were encountered which appear to be in the Vigo shale—one at the head of Tangob Creek, north of Cabongahan, and the other on Dumalog Creek at the head of Guinhalinan River. The Tangob exposure is in the upper part of the series, a few meters below the Canguinsa sandstone; while the outcrop on Dumalog Creek appears to be considerably lower in the Vigo shale, several hundred meters below the base of the Canguinsa sandstone. Elsewhere, no agglomerate was noted except as float, and it is not certain that the Dumalog agglomerate is in place.

The thickness of the Vigo shale is unknown. An apparent thickness of about 1,400 meters is revealed in the Matataha

River section, the section on Malipa Creek in the southern limb of the Malipa anticline shows 800 meters of Vigo shale, and the section on Guinhalinan River indicates 600 meters. None of these sections exposes the base of the formation. The apparent thickness of the sections as measured along the outcrop may be in excess of the actual thickness as a result of superficial expansion of the beds or of the repetition of beds from faulting or close folding.

As is indicated on the geologic map, the Vigo shale is prominent in the north-central portion of the field. A smaller area is exposed along the southwestern coast. The deeper valleys have uncovered Vigo shale in other parts of the peninsula.

A small number of fossils were observed in the lower part of the Vigo, and the shale in the Bacau stage and the overlying conglomeratic sandstone are fossiliferous. The specimens are fragile and upon removal disintegrate readily, in a manner that suggests the effects of calcination. Frequently they are enveloped in a film of oil or grease as are the shells in the clay beds of the Canguinsa sandstone.

At fossil locality 11 on Dumalog Creek, fossils were found in bedded blue-black shale which is placed in the Bacau stage of the Vigo. This locality is on the trail from San Narciso to Mulanay on the west slope of Cambagaco Ridge at an elevation of 130 meters.

The stratigraphic relations are shown in Table XIII.

TABLE XIII.—*Geologic section downstream on Dumalog Creek.*
Fossil locality 11.

Formation.	Description.	Thickness.
		Meters.
Malumbang series and Canguinsa sandstone.	In the east slope and the crest of Cambagaco Ridge, limestone and sandstones are encountered in obscure relations. The general dip is eastward at an angle of about 30°.	200
	Gray to brown sandstone and fine conglomerate. Strike, north 50° west; dip, northeast, 45°.	10
	Black laminated clay or shale. Carbonized leaf-impressions and lenses of lignite, 5 millimeters thick.	20
Vigo shale _____	Gray to brown sandstones, massive, coarse grained _	10
	Bacau stage; thin-bedded shale with subordinate sandstone beds; dip 65° northeast; fossils found in the shale beds.	50
	Concealed interval _____	400
	Volcanic agglomerate, a single small outcrop in thin-bedded shale and sandstone.	_____

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Among the fossils collected the following were identified.

Fossils collected at locality 11.

Conus loroisii Kien. +	*Tapes rimosa* Phil. +
Pyrula sp.	*Conus striatellus* Jenk.
Arca sp.	*Conus hochstetteri* K. Mart.
Natica sp. indet.	*Fusus* sp. indet.

In a specimen of the conglomeratic sandstone which occurs in the upper part of the Vigo shale in Matataha Valley one species of *Mitra* and one of *Pyrula* were noted. *Globigerina* (Plate V) was found in the Vigo shale, more abundantly in the Bacau stage.

The general aspect of the fossils in the Bacau stage of the Vigo shale is very similar to that of the fossils in the base of the Canguinsa sandstone (Plate IV). The age of the beds is not fixed definitely, but the fresh appearance of the shells and the number of species still living make it improbable that they represent a period earlier than the Miocene. The base of the series may be as old as the Oligocene.

The Vigo shale includes all the known petroliferous horizons in this field. Seeps of petroleum and inflammable gas occur in the Bacau stage, generally within a few meters below the base of the Canguinsa sandstone; on Malipa Creek, however, traces of oil and gas are observed with 250 meters of Vigo shale exposed above them. The occurrence of petroleum is discussed on page 349.

As to the character of the rocks which occur below the Vigo shale, there is little evidence. The shale may rest directly upon the basal diorite which is cited by Becker [14] as probably the oldest formation in the Philippine stratigraphic column, or upon a sedimentary series older than the Vigo shale. Elsewhere in the Philippines, Miocene shale has been found in some cases to overlie Eocene shale and limestone, in others to rest immediately upon a base of older igneous rocks, and rarely to be underlain by older "slates" which are probably of Jurassic age.

At Peris, about 25 kilometers northwest of San Narciso, the common basal diorite occurs, overlain unconformably by the Cudiapi sandstone. Toward the south, successively older formations, down to and including the Vigo shale, at least, undoubtedly overlap the diorite base just as the Cudiapi sandstone does at Peris. Possibly sedimentary rocks older than the Vigo shale intervene between it and the lowest parts of the diorite floor.

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[14] Becker, G. F., *21st Ann. Rep. U. S. Geol. Surv., 1899–1900,* pt. III (1901), 24 of reprint.

Volcanic agglomerate.—In the northeastern part of the area shown on the map several exposures of andesitic agglomerate were encountered. Two outcrops were found at different horizons in the Vigo shale and one in the base of the Canguinsa sandstone.

The most extensive outcrop is a conical hill about 1 hectare in area and 50 meters high. The form is not unlike that of an old volcanic plug, but may be due entirely to the work of erosion. The material is principally agglomerate; but apparently massive andesite is to be seen in the central part of the exposure, while an intermediate zone consists of andesite in which the fragments occur in a stony crystalline matrix. The other exposures are also conical in form, but are much smaller and consist entirely of agglomerate, angular fragments of andesite, varying in weight from a fraction of a kilogram to 10 kilograms, embedded closely in andesitic tuff. There is a suggestion of bedding in the agglomerate in the base of the Canguinsa sandstone on Vigo River. The outcrops are gray to dark brown, and are weathered in a manner that leaves the fragments protruding irregularly from the matrix. The agglomerate appears to be interbedded in the shale, but the contacts are obscure and it is not certain that it does not lie upon an eroded surface of shale.

Near the village of Bato, bowlders of fragmental rocks, probably volcanic agglomerate, were observed in which sedimentary types—sandstone and shale—are most prominent, but are accompanied by andesite. A thin section of fragmental andesite from this agglomerate was examined under the microscope. The texture is decidedly porphyritic with a large proportion of phenocrysts, consisting of dark green to brown hornblende and plagioclase feldspar crystals. In the subordinate groundmass occasional crystals and fragments of magnetite are scattered. The petrographic character indicates an extrusive, certainly not a plutonic and probably not an intrusive, rock. A more homogeneous specimen of andesite taken from the main exposure on Tangob Creek shows similar characteristics. It is porphyritic, one of the hornblende phenocrysts measuring more than 1 centimeter in length. The hornblende crystals are more abundant than in the previously described rock, and show well-defined reaction rims.

The several outcrops of volcanic agglomerate occur along a line roughly parallel to the general strike of the sedimentary beds. They are of small area, the distances between them are relatively great, and there is little reason to believe that they

represent a continuous formation. The fact that parts of the formation are typical agglomerate with a tuffaceous matrix makes it very improbable that these outcrops represent an intrusion. The material appears to be clearly of volcanic origin and to consist principally of fragmental ejecta. Whether each outcrop represents a center of local effusion, or is the remnant of a larger sheet of agglomerate which came from a distance and was interbedded in the shale, cannot be decided without further investigation.

The importance of the igneous rocks relative to the accumulation of petroleum is problematical. Traces of oil and gas are found in the shale on Tangob Creek adjacent to the largest outcrop of agglomerate. If the observed outcrops mark local centers of extrusion, then the beds stratigraphically below them must be pierced and more or less broken by the volcanic vents from which the agglomerate was thrown out. In the light of drilling experience in most large oil fields this condition probably would be looked upon with disfavor. However, it is well known that large flows of oil have been obtained in Mexico near volcanic rocks which have come up through sedimentary beds, and it has been suggested [15] that the vulcanism has supplied the conditions necessary for the accumulation of the petroleum. Thus, even if the agglomerate in Tayabas has been extruded locally, it should not condemn any part of the field, and may have had a desirable effect.

If the agglomerate has not been extruded locally but has been thrown out from a distant center, its presence probably has little bearing on the question of petroleum exploitation. It is conceivable, of course, that an impervious sheet of interbedded agglomerate might influence the accumulation of any petroleum in the rocks below it, but the data available do not warrant any procedure based on this possibility.

On the whole, in view of their limited extent and of their probable extrusive origin, it may be concluded that the igneous rocks have no important bearing, either favorable or unfavorable, on the possibilities of this oil field.

STRUCTURE

General.—Bondoc Peninsula occupies a geanticlinal zone in the folded strata of southern Luzon and the adjacent islands. Ragay Gulf, lying east of the peninsula and between it and the larger peninsula of southeastern Luzon, probably occupies an

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[15] Garfias, V. R., *Journ. Geol.* (1912), **20**, 2, 666.

adjacent geosyncline.   The elevation of Bondoc Peninsula above sea level is due, in part at least, to its anticlinal structure.

In the general arch which the strata form across the width of the peninsula there are minor undulations which have been studied as individual folds.   Among these folds the anticlines are more sharply defined, and hence more easily traced, than the synclines.   Because of this and of their probably greater importance in connection with petroleum accumulation the anticlines have received more attention than the synclines.   In connection with the discussion of the structure reference should be made to the geologic sections shown on the map.

Confusing irregularity is encountered in the strikes and dips of the Vigo shale in parts of the field, particularly in the upper valley of Mulanay River and in a small area north of Cabongahan.   At the latter place along small streams, outcrop after outcrop was examined, the strikes and dips of which are utterly at variance, even when all but the most reliable-appearing exposures are ignored.   Because of this fact, the structural relations have proved locally undeterminable.

The Vigo shale is a thinly laminated and nonfrangible formation which would scarcely be maintained as a competent arch in folding, but probably would break and move upon itself where ⸱ the strains were most severe, leaving the strata in confused disorder at these points.   In the crest region of the Central anticline the shale is much disturbed, and extreme confusion in the attitude of the beds is encountered near the intersection of this fold with the minor cross anticlines, while the strikes are regular and uniform only in the limbs or far down in the core of the anticline.   The squeezing and distortion, due to close folding in a formation structurally incompetent, together with superficial displacement and caving due to erosion, are probably the main causes of the observed irregularity in the Vigo shale.

Unconformities.—In addition to the unconformity at the base of the recent deposits on Bondoc Peninsula there is considerable discordance between the Canguinsa sandstone and the Vigo shale.   No exposures were found showing an eroded surface of the Vigo shale beneath the Canguinsa sandstone, but in regions where the inclination of the beds is steep an abrupt increase in the angle of dip is apparent on passing from the higher to the lower formation, although the strike remains more or less constant.

The change in the degree of inclination of the two formations is best illustrated by the conditions on the upper part of Malipa Creek where steeply dipping Vigo shale is overlain by almost

horizontal Canguinsa sandstone. Similar relations are to be observed along the western base of Mount Cambabaco.

Overlap on the part of the Canguinsa sandstone, which would be expected if this member were laid down upon the truncated edges of the Vigo shale, is not very extensive. At a number of places the Canguinsa sandstone is encountered above approximately the same horizon in the Bacau stage of the Vigo shale. Elsewhere, as is shown in the section on Dumalog Creek, page 333, and the section on Guinhalinan River, page 322, more or less sandstone or sandstone and fine conglomerate, bedded conformably with the Vigo shale, intervene between the Bacau stage and the Canguinsa sandstone.

The volcanic agglomerate might be taken as evidence of a distinct break in the process of sedimentation if it occurred uniformly between the discordant members, but the outcrops do not appear to lie along the unconformity nor to be confined to a single horizon. It is possible, however, that more detailed work would show that the agglomerate does occur along the unconformity, and thus indicate a decided break between the Vigo shale and the overlying formations. In the data at hand, however, the overlap of the Canguinsa sandstone and the steeper dips in the Vigo shale are the principal evidences of unconformity.

If the steeper angle of dip in the Vigo shale, as compared with the overlying formations, is accounted for by assuming that the later rocks were laid down on an eroded surface of previously folded Vigo shale and were themselves thrown into folds subsequently, two periods of folding are involved with a remarkable coincidence in the position and trend of the later folds along the axes previously established in the Vigo shale. A theory of a single period of folding is simpler and is in accord with the observations in the field, if mechanical unconformity, resulting from the different frangibility of the Vigo shale and the overlying formations, be admitted as adequate to account for the overlap of the Canguinsa sandstone and the lesser inclination in the beds above the Vigo. On the other hand, there is evidence in the sandstones and conglomerates immediately above the Bacau stage that the seas became very shallow before the deposition of the Canguinsa sandstone began, and it is possible that the Vigo shale emerged from the sea and became subject to erosion, although positive evidence of erosion is lacking. The fossils in the two formations indicate that there was no great interval of time between them.

Whether the unconformity is one of erosion or of mechanical discordance only, the Canguinsa sandstone appears to overlap

the Vigo shale, and this is of practical importance in that the overlap may conceal petroliferous members of the Vigo shale above the Bacau stage.   The conclusions in this report regarding the general lines of structure—the position of the main anticlines etc.—are to a degree independent of the unconformity, since the larger folds are approximately coincident above and below the discordance.

Central anticline.—The principal structural feature of Bondoc Peninsula is the series of folds whose trend conforms roughly to that of the peninsula.   These folds are made up of broad shallow synclines and narrow acute anticlines.   Subordinate anticlines occur near both lateral coasts, and a larger anticline designated as the Central anticline marks the axis of the peninsula.

The Central anticline is asymmetric in that the eastern limb is more highly inclined than the western.   The fold is sharp, especially in the lower strata which are vertical along the axis, and about 25 kilometers in length.   The general strike of the axis—north 30° west—is not maintained with absolute uniformity, but becomes almost north and south toward the southern end of the peninsula.   A general southerly plunge of the anticlinal axis is indicated by the fact that, from north to south along the axis, beds successively higher in the stratigraphic column are encountered at the same elevation.

In the northern part of the field the axis coincides with the summit of the low divide between Sibuyanin and Vigo Rivers. From this point it follows more or less closely a straight line south-southeast as far as Cuyocuyo Creek.   Farther south the crest of the fold appears to coincide with the upper part of Canguinsa River, so that south of Cuyocuyo Creek the axis must trend about north and south.   Beyond Bacau, the sharp fold dies out, and was not certainly identified farther south; although the gentle overturn of the strata, indicated in the western part of Amoguis Valley, probably marks its continuation.   North from the divide between Matataha and Sibuyanin Rivers the Central anticline can be traced as far as the eastern slope of Mount Maclayao.   In Mount Maclayao, Vigo shale is encountered, striking east-northeast and dipping steeply to the south, and at the intersection of this line of strike with the Central anticline the identity of the latter is lost in a confusion of varying strikes and dips.

In the axial portion of the fold at the head of Sibuyanin River, vertically dipping beds of Vigo shale are exposed.   In the western limb the dip decreases rapidly, and within a few hundred meters to the west-southwest of the axis it amounts

to only 45°, while 2 kilometers from the axis the dip—west-southwest—is as low as from 15° to 20°.   Still farther west the beds lie horizontal in the syncline between the Central anticline and the Ayoni anticline.   In the opposite or eastern limb a dip of from 55° to 65° to the east-northeast persists for a distance of 1 kilometer to the eastward from the axis.   Farther east, the relations are uncertain and are discussed in connection with the Malipa anticline (page 342).

To the south the western limb can be identified in the beds exposed along the eastern slope of Cudiapi Range.   The upper part of the Vigo shale, which outcrops along Cambagnaon and Cuyocuyo Creeks, dips from 25° to 30° to the west-southwest; but the beds lower in the formation and nearer the axis of the anticline are steeper, dipping from 60° to 70°.   The Canguinsa sandstone which has been removed by erosion farther north reappears in Cudiapi Range, overlying the Vigo shale and dipping
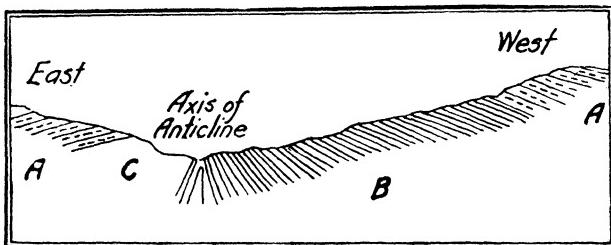
FIG. 1. Diagrammatic section across axis of central anticline in the upper valley of Malipa Creek. (*a*) Canguinsa sandstone; (*b*) Vigo shale; (*c*) concealed.

at low angles to the west-southwest.   In the eastern limb of the fold in this vicinity the Canguinsa sandstone is encountered very close to the axis dipping gently to the eastward.   The nearest exposures of the underlying Vigo shale are vertical, or dip at high angles to the east in the axial portion of the fold. There appears to be insufficient room between the axis and the Canguinsa sandstone in the eastern limb for a thickness of Vigo shale equivalent to that exposed in the western limb.   The relations are shown in text fig. 1.

Possibly faulting has occurred in the plane of the axis as a result of sharp folding, and the western limb has been thrust upward along the fault.   Such a condition would explain the position of the lower part of the Vigo shale in the western limb so nearly in contact with Canguinsa sandstone in the eastern limb.

In the headwaters of Canguinsa River an exposure of Vigo

shale was observed dipping 45° to the westward, the later formations lying above it and dipping in the same general direction at a lesser angle.   South of Balinsog, as far as Bacau, the Canguinsa sandstone is intact across the axis of the anticline, and the upper formations dip gently away to the east and west on either side of Canguinsa River.   The Bacau stage of the Vigo shale is exposed in the river at Bacau, dipping 55° east-northeast; and above this exposure, in the eastern wall of the valley, the Canguinsa and Malumbang formations are encountered dipping at low angles to the eastward.   Up and down stream from the outcrop of Vigo shale at Bacau the relations are concealed; the river swings to the southwest at this point, and the next exposures downstream are of Canguinsa sandstone dipping gently westward.

The existence of a minor cross-anticline, the axis of which coincides roughly with the lower part of Canguinsa (Silonguin) River, is suggested in the discussion of the geologic control of the topography.   In the upper part of the gorge, which Canguinsa River enters after its abrupt turn to the southwest, the Canguinsa sandstone dips to the north of west, while farther downstream the direction of dip has swung to south of west, indicating that the river in its course to the southwest has passed over the axis of a small anticline trending east and west in the general western limb of the larger fold.   In a profile view of a cross section of the gorge, which may be obtained from Mount Anuing, the effect of this small anticline may be detected in the slope of the land surface to the north and south away from the rims of the gorge.   The northerly dip of the beds in the hills along the north edge of Malumbang Plain probably represents the northern limb of this cross-flexure.

It is probably due to the presence of the cross anticline at Bacau that the Vigo shale is thrown up so as to appear again at the surface after having been carried down by the general southerly plunge of the axis, far enough to escape erosion at the same elevation farther north.

Structure in the region north of the Central anticline.—In Sobo Creek, which drains a part of the western slope of Mount Maclayo, strata in the upper part of the Vigo shale were observed striking north 65° east and dipping 65° to the south.   On Mulanay River, above the point where the tidal influence ceases, numerous outcrops of Vigo shale are to be seen in a majority of which the strikes are a few degrees north of west, and the dips are either vertical or steep both to the north and south.   A

smaller number of exposures show the usual north-northwest strike with dips to the west or occasionally to the east.

Northeast of this region, between Guinhalinan River and the eastern coast, the formations are found in their usual relations—striking north-northwest and dipping to the east from 35° to 40°. On Ajus River to the northwest, likewise, the prevailing strike conforms to the established order; but the position of the beds indicates an overturned fold with the lower part of the Vigo shale, which dips to the eastward at angles of from 60° to 90°, recumbent upon the sandstones and conglomerates in its upper portion. The overturn does not persist through the younger formations apparently, since these are found in the range of hills along the coast, dipping at an angle of about 45°, westward.

Inland from Catanauan and northwest of Ajus, the limestone in the coastal ridge dips to the southwest at an angle of about 45°. In the valley east of this ridge, Vigo shale is exposed, dipping 50° to the southwest. Thus, the slight overturn at Ajus appears to adjust itself along the strike of the formations; the strata resume a steep southwestern inclination, northwest of Ajus, corresponding to the lesser dip in the same direction at Matataha and Ayoni, southeast of Ajus.

Summarizing the discussion of the structure north of the Central anticline, the seaward dipping formations near each coast may be interpreted as evidence of a general arch across the width of the peninsula. The relations in the crest portion of the suggested arch are complicated and obscure. It appears that folding at right angles to the general structural lines has occurred, together with close folding and overturns along the main lines of structure.

Malipa anticline.—The strikes and dips in the Vigo shale near Cabongahan indicate the presence of a subordinate anticlinal undulation in the eastern limb of the Central anticline. The smaller fold, known as the Malipa anticline, trends north 65° to 70° west, making an angle of about 40° with the axis of the Central anticline. Its crest is roughly coincident with the lower course of Vigo River. The fold is well developed in the Vigo shale, but is only faintly reflected in the younger formations lying in the ridge near the eastern coast. In the southern limb of the anticline, along Malipa Creek, a thickness of 800 meters of Vigo shale is exposed, dipping to the south-southwest at an angle of about 55°. Above the Vigo shale, the Canguinsa sandstone appears, overlain by patches of coralline limestone.

Only a few exposures were observed which can be referred

to the northern limb of the Malipa anticline. These are found along Vigo River, and dip about 45° to the north-northeast. Farther north the dips and strikes are much confused, and the structure is not clear. The volcanic agglomerate is encountered at the head of Tangob Creek. In this vicinity the Vigo shale dips steeply to the east-northeast in perhaps a majority of the exposures, but its relations are not uniform.

Bato anticline.—Near the small village of Bato, north of Cabongahan, the lay of the beds indicates a local anticline in the Vigo shale, the axis of which is roughly parallel to the Central anticline. Like the Malipa anticline this fold appears to be a minor overturn in the general eastern limb of the Central anticline. It is a sharp flexure, the strata in each limb dipping at angles of 60° or more, but is persistent over a length of a few hundred meters only. The stream between Bato and the ridge to the east appears to follow the axis of this anticline. The Bacau stage of the Vigo shale is exposed along its crest and dips away from the stream line on either side. The upper formations appear on top of the Vigo shale in the eastern limb, forming the high ridge between the anticline and the eastern coast. The dip in the uppermost beds is from 30° to 45° east-northeast. Pusgo Bay which lies off the eastern coast at this point occupies a syncline, and San Narciso Peninsula, east of the bay, is a monocline dipping gently westward toward this syncline. West of the axis of the Bato anticline only Vigo shale is exposed and the westerly dip of its beds persists for a short distance only, beyond which the shale dips steeply to the east-northeast, marking the eastern limb of the Central anticline.

In the Florence, Colorado, oil field,[16] the stream lines are sometimes marked by small sharp anticlines, which are attributed to purely superficial phenomena, such as the expansion of rocks through weathering and consequent thrust of surface beds into the valleys formed by streams. It is possible that the Bato anticline is of this type, but the fact that petroleum is found along its crest argues that it is more than superficial in effect, since petroleum is found usually in true anticlinal zones, elsewhere in the field.

Ayoni anticline.—Inland from the villages of Ayoni and Bondoc on the west coast, the dip measurements and the hill forms reveal an upward flexing of the strata along a line directed north 35° west. This axis is about 1,200 meters and 2,000 meters from the coast at Ayoni and Bondoc, respectively. The

[16] Washburne, C. W., *Bull. U. S. Geol. Surv.* (1909), **381**, 49.

gentle anticline which is defined along it becomes evident a short distance south of Matataha River and persists over a length of 10 kilometers to a point east of Bondoc. Sandstones, about 300 meters in thickness, are exposed in the western limb at Ayoni, dipping from 35° to 40° west-southwest and overlain conformably by limestone. The sandstones probably represent the Canguinsa and part of the Vigo formation, and the limestone, the lower stage of the Malumbang series. East of the axis in the west slope of the Cudiapi Range, a similar section culminating in limestone and calcareous sandstone is revealed. The inclination of the strata in the eastern limb is generally less than 15°.

Between the northern end of the Ayoni anticline and the cross fold at Mulanay, an area in which the strata are horizontal intervenes. Mount Cancalao, left by erosion in the Matataha Valley, affords a section of horizontal strata in which bluish black shale at the base is covered by beds of sandstone, sandy micaceous shales, and sandstone conglomerate with a total thickness of nearly 200 meters. On the coast west of Mount Cancalao, the strata dip seaward as they do at Ayoni, and precise measurements would probably reveal a slight anticlinal fold between the mountain and the coast.

South of the Ayoni anticline as far as Silonguin (Canguinsa) River, the structural relations are uncertain. The identity of the smaller fold is lost in a general slight dip to the southwest, which probably marks the western limb of the Central anticline.

Cudiapi syncline.—The Cudiapi syncline is a shallow structural basin lying between the Central and Ayoni anticlines. The rocks have been preserved from erosion within this zone and form the rather flat-topped Cudiapi Range extending southeast from the headwaters of Sibuyanin River to Silonguin River. The Canguinsa sandstone and the Lower limestone of the Malumbang series are exposed over most of the surface, but remnants of the Cudiapi sandstone occur locally.

Maglihi anticline.—The Maglihi anticline—marked by Mount Maglihi, a conspicuous peak formed by the almost vertical strata in its crest—is an acute upward flexure in the eastern part of the monocline which persists with a gentle eastward dip across the southern end of the peninsula. The anticline is most clearly revealed in the vicinity of Mount Maglihi, where the axis strikes north 5° east, and the eastern limb is much steeper than the western. South of the mountain, the axis plunges so that the fold is barely perceptible in the strata near the southern coast. Northward, it can be traced with some difficulty for several kilometers and probably continues to Bahay where a similar fold

is indicated.   At Bahay, however, the western limb is not clearly defined in the younger formations and the axis has changed its direction to the north-northwest, in conformity with the general strike in the field.

In the region of Mount Maglihi, the western limb of the fold can be identified without difficulty.   For several hundred meters west of the axis, the Upper limestone and Cudiapi sandstone dip from 15° to 20° to the westward, reversing the monoclinal slope from the summit of Mount Banaba and forming the eastern limb of a shallow syncline occupied by Malumbang Valley.   The Vigo shale, exposed at the oil seep near Banco, likewise dips to the westward, but at a greater angle (45°).   North of Banco, the crest of the fold is less deeply eroded, and the base of the Canguinsa sandstone is not uncovered.   On Mount Maglihi and Mount Morabi, which are in the eastern limb close to the axis, the Canguinsa sandstone dips generally about 55° to the east, but locally it is vertical, or even overturned slightly to the west. The Canguinsa sandstone is calcareous in this locality, and in the summits of the hills just mentioned contains sandy limestone a few meters thick (Table XI).   In the Malumbang series, lying farther from the axis in the eastern flank of the fold, the angle of dip decreases regularly to about 30°.

The more highly inclined strata east of the anticlinal axis are exposed in apparently greater thickness than is evident in the western limb, and the lower part of the Canguinsa sandstone in the eastern limb is brought into close association with the Malumbang series in the opposite limb.   The relations suggest faulting along the strike of the beds in the crest of the anticline with an upward thrust of the eastern limb, but in the absence of precise measurements actual movement along the suspected fault plane cannot be established.

A commonly stated law applying to asymmetric anticlines is that the active thrust came from the side of gentler slope, that is, in the case under discussion, from the west.   If the force came from the west, the eastern limb could scarcely have been thrust up over the western.   Since the evidence of the overthrust of the eastern limb is not conclusive, and the law as to the direction of the active forces—while not of universal application—is assumed to hold true generally, the occurrence of actual displacement along a fault plane in this fold must be questioned.

At Bahay the relations are similar to those in the region just described.   Bahay River, flowing north, and Milipilijuan Creek, flowing south, have cut out a deep valley along the axis of the flexure and parallel to the coast line.   Between this valley and the

coast is a ridge in which the strata from the Canguinsa sandstone to the Upper limestone are found dipping from 30° to 40° east-northeast. The top of the Vigo shale, exposed at several places along Bahay River and Milipilijuan Creek, is the lowest horizon reached by erosion. Most of the outcrops are in the eastern limb of the fold and dip 55° east-northeast.

West of Bahay River, which marks the axis of the flexure, the formations still dip to the eastward, but at very low angles. At the mouth of Apad Creek, which flows into Bahay River from the west, the Canguinsa sandstone dips slightly eastward. Farther up the creek, the Cudiapi sandstone appears above the Canguinsa and dips to the southeast from 15° to 30°. Several of the exposures of Vigo shale in Milipilijuan Creek dip to the westward, and it is probable that the Vigo shale forms a true anticline at Bahay with dips to the east-northeast and to the west-southwest away from the axis. The flexure in the upper, less easily folded, strata is anticlinal in character in that the strata are differently inclined on either side of its axis so as to form an arch, although the dips are all in a single general direction (eastward). In these beds there is only an abrupt increase in the eastward dip along a line which becomes the axis of an anticline farther south.

There is evidence of displacement at Bahay similar to that near Mount Maglihi. Acute folding with erosion along the crest might account for the observed relations, but an accompanying upward thrust of the eastern limb along a fault plane is indicated. The objection to the theory of an overthrust of the eastern limb at Mount Maglihi, discussed on page 345, applies with equal force to the conditions at Bahay.

Banaba monocline.—An extensive monocline, the general northeast dip of which is conspicuous in Mount Banaba, forms the southern portion of the peninsula. Based on rather meager evidence, a minor overturn in the region of Sili and Tala and a close fold near the southwestern coast are shown in the geologic section (Map I) as modifications of this structure.

The strike of the beds varies in different parts of the area. On Mount Banaba it is north 30° west, near Bondoc Head it is north 50° west, and in the western part of the monoclinal area it is north 15° west, parallel to the adjacent coast line. From Mount Banaba to Sili the average dip is probably 15°, and in the section between these places only the strata in the Malumbang and Canguinsa formations come to the surface. It it surprising, in view of the general northeast dip, that the upper part of the Vigo shale is not exposed in the deep valley of Amoguis River. The difference in elevation between the summit of Mount Banaba and the

floor of the valley is great enough that the entire thickness of the strata above the Vigo shale should be included in the section exposed in the eastern wall of the valley, unless the upper formations are thicker here than they were found to be farther north.

On Sili Creek, a few hundred meters south of Sili, the Bacau stage of the Vigo shale is exposed, but only over a small area, and west of Sili the upper formations reappear and are found in the floor of the next valley to the westward, at an elevation as low as that of Sili Creek. This condition suggests that the general northeast dip of the strata is reversed to a westward dip for a short distance west of Sili. Faulting might produce the same effect, but there is no evidence of faulting in this vicinity. Neither were the suggested westward dips detected at Sili proper, but north of Sili, at Tala, dips to the west are found in the upper formations. On the basis of this evidence, a small anticline is shown along this line in the geologic section. It will be noted that this fold is approximately in the position which a southward continuation of the Central anticline would occupy.

West of Tumbaga River, the Vigo shale reappears, dipping 35° east-northeast, and the exposure extends southwest to the seacoast. The dip of the beds increases regularly toward the southwest, becoming almost vertical at the eastern base of the chain of hills along the western and southwestern coast. On top of Bondoc Head the Canguinsa sandstone and part of the Malumbang series occur, lying almost horizontal. West of Bondoc Head on the seacoast, the Vigo shale, dipping 30° to the northeast, is encountered again. In the summit of the ridge near the mouth of Bataniog Creek are sandstone and sandy conglomerate, similar to the strata in the upper part of the Vigo shale near Matataha. These beds dip to the east at an angle of 70° and strike about north.

If the monoclinal structure persists to the southwestern coast, Bondoc Head should consist of steeply inclined beds of Vigo shale. Instead, the summit of this mountain is covered with younger formations. At the mouth of Bataniog Creek, again, are the sandstones and conglomerates which are found usually at the top of the Vigo shale. If there is no reversal in the general monocline, these beds are out of their usual stratigraphic position, and the indicated thickness of the Vigo shale is at least 3,600 meters. Both these conditions seem improbable, and a close fold recumbent to the southwest, as shown in the geologic section, is a more reasonable interpretation of the data in hand. The relations may be complicated by faulting analogous to the suspected faulting in the Maglihi anticline.

GEOLOGIC HISTORY

The southern part of Bondoc Peninsula appears to have been the site of shallow water deposition during the larger part of Miocene time. Of the conditions prior to the Miocene, there is little evidence. Quartz-veined diorite and schist, both older than the Miocene, occur farther north on Bondoc Peninsula and probably continue into the region under discussion, lying beneath the sedimentary strata. That rocks of this character formed a part of the land mass from which the sedimentary beds in the oil field were derived is proved by the presence of rounded quartz, diorite, and schist fragments in the sandstone and conglomerate members of the series.

The fact that the highest beds are folded in fair accord with those at the base of the stratigraphic column indicates that the major part of the folding occurred after the close of the Miocene and the completion of sedimentary processes in this region. From the steeper dip in the eastern limbs of most of the anticlinal folds, it might be inferred that the folding stresses were transmitted from the west. Not all the evidence obtained confirms this view, however, and without more data a conclusion is hardly justified.

The interbedding in thin layers of fine-grained shale, sandy shale, and sandstone shows that the Vigo shale formed in moderately shallow water. The thickness of the series and the regularity of the beds imply uniform conditions over the area throughout which they are distributed. Continued deposition of sediment in shallow water, until a succession of strata equal in thickness to the Vigo shale is built up, would appear to require an accompanying gradual subsidence of the sea floor. The less clearly defined bedding planes and the increased proportion of fine sediment in the Bacau stage, as compared with the lower part of the Vigo shale, suggest that deposition became more constant and regular and that the water became deeper before the beds in this stage were deposited; however, shallow water conditions must have prevailed at the close of the period when the sandstones and fine conglomerates were laid down. The Vigo shale may have emerged above sea level, entirely or in part, and have been subject to erosion before the succeeding beds were deposited. A period of volcanic activity in or adjacent to the region, at about this time, is attested by the presence of the volcanic agglomerate near the top of the Vigo shale.

The thick massive beds of fine sediment in the Canguinsa

sandstone appear to have been formed as a continuous deposition in deep or quiet water. Parts of the formation, however, are coarse grained and were probably laid down in shallow seas similar to those which must have prevailed during the deposition of the Malumbang series. The growth of coral in the limestones in the Malumbang series indicates that the water was clear at times toward the end of sedimentation.

The Pleistocene and Recent deposits of volcanic tuff, which are extensive in the neighboring territory of southwestern Luzon, do not reach as far to the southeast as Bondoc Peninsula. Subsequent to the Pliocene, apparently, the mass of Bondoc Peninsula has been above sea level, and subject to erosion which has been very extensive and has removed great thicknesses of strata.

OCCURRENCE OF THE PETROLEUM

The petroleum on Bondoc Peninsula appears as seepage from the floors or sides of streams. At some places the oil rises spontaneously and floats away on the surface of the water. More commonly it appears only after the prospector has disturbed the rocks at the bottom of the stream. Digging in the shale of the Bacau stage where it has been freshly exposed by stream erosion generally yields small quantities of petroleum. The oil is invariably accompanied by inflammable gas, and in a number of instances inflammable gas is encountered in the absence of oil. At none of the seeps is there evidence of a large flow of oil at the surface. To collect as much as a liter of oil from any of the seeps involves a considerable amount of work in turning over the rocks and stirring up the mud in the streams along which the oil is found. The petroleum contains a large proportion of volatile constituents, and all trace of oil is lost soon after it appears on the surface. There is no discoloration of the ground around the seeps, but a scum gathers on the water and on stones or sticks in the water for a short distance downstream from an oil seep. The proximity of a seep is usually manifested first by the odor of kerosene which is evolved rather than by visible evidence of the petroleum.

In all cases where oil has been found, it occurs in or near the Bacau stage of the Vigo shale, more or less closely below the Canguinsa sandstone in the stratigraphic column. The seep on Malipa Creek, near Cabongahan, is at the lowest horizon in the Vigo shale at which oil has been encountered. Here Vigo shale some 250 meters thick intervenes between the oil seep and

the base of the Canguinsa sandstone. In the lowest exposed portions of the Vigo shale but little oil is to be observed.

The oil is associated with the shale, rather than with the sandstone, where sandy layers are interbedded, and in several cases it comes directly from the shale. The absence of oil in the interbedded sandstone at the outcrop may be due in part to the rapidity with which it volatilizes and thus escapes from porous media.

Petroleum seeps were encountered at Banco, at Bahay, and on Milipilijuan Creek along the Maglihi anticline; on Sili Creek, a branch of Pagsanhan River; at Bacau on the Central anticline; on Malipa and Tangob Creeks in the vicinity of Cabongahan; at Bato, north of Cabongahan; and on Ajus River in the northeastern part of the field. Traces of oil and inflammable gas were detected at several other places, including the outcrops of Vigo shale dipping steeply south-southwest on the upper part of Sobo Creek, south of Mulanay.

PETROLEUM AT BANCO

Petroleum is found at Banco near the head of Canibo Creek which flows to the south from the small valley in the crest of the Maglihi anticline. The seep is at an elevation of about 200 meters. A strong odor of kerosene reveals the presence of the oil, which on closer inspection may be seen to rise in globules from the bottom of the small stream and to float away in films on the surface of the water. The seepage is accelerated by probing in the rocks and débris in the bed of the stream, and a small quantity of petroleum can be collected by skimming the globules and films from the water. The underlying rocks are concealed at the immediate point of escape, but 20 meters downstream bedded petroliferous shale and sandstone, belonging to the Bacau stage of the Vigo shale, are exposed. These beds dip to the west at an angle of 45°, so that the seep is in the western limb of the anticline. The wall of the valley rises steeply on the west to an elevation of more than 300 meters, and is made up of the rocks of the Canguinsa sandstone and Malumbang series.

About 200 meters south of the main seep, oil may be detected in blue to black petroliferous shale on the floor of an arroyo in the western wall of the valley. Maalat Creek, an adjacent tributary of Canibo Creek, contains salt water, as the native name, "Maalat," implies.

PETROLEUM AT BAHAY

The strongest seep in the Bondoc field is, perhaps, that at Bahay, the drilling site of the Bahay Valley Oil Company on Bahay River. Bahay River is about 15 meters in width at this point, and the oil appears at numerous places over the whole surface of the stream throughout a length of 50 meters. It comes up spontaneously, accompanied by bubbles of inflammable gas, and forms an extensive surface film. An unusual cloudiness in the water is commonly attributed to the presence of the oil. The river bed is covered by pebbles and small bowlders of limestone eroded from the Lower limestone which is exposed several hundred meters upstream, and the oil is trapped beneath the larger rocks and escapes to the surface after the temporary reservoirs which these afford are filled. The elevation of the seeps above sea level is about 50 meters.

The formation is concealed within the area covered by the seeps. Fossiliferous sandy clays, believed to represent the Canguinsa sandstone, were observed upstream—about 300 meters south of the seep. The structural relations of this outcrop could not be determined since no planes of stratification are discernible. North of the seeps—approximately 150 meters downstream—imperfectly bedded shale occurs, dipping to the east-northeast at an angle of 55°. This shale is sandy, blue to black in color, and contains carbonized impressions of leaves and broken plant stems. From the position and dip of this shale it appears that the seeps are probably in the eastern limb of the anticline and from the relations elsewhere it is evident that they are very close to the axis.

Two wells have been drilled near the seeps. The first well, Bahay 1, is located a few meters west of the river bank opposite the point where the seeps are most numerous. It was drilled by hand in 1906 under the direction of Mr. E. W. McDaniel, managing director for the Tayabas Mutual Oil Association. It is cased with 4-inch pipe, and reached a depth of 38.7 meters. A record of this well is not available, but the following data appeared in the Far Eastern Review:[17]

The first oil sand occurred at a depth of 62 feet and continued through six feet to a depth of 68 feet. From this strata using the mud bailer as a pump, 46 gallons of crude oil of an excellent quality was secured in one day's work, * * *. Owing to the crumbling nature of the formation above

[17] *Loc. cit.*

and below, this oil bearing strata was cased out and the well continued to its present depth of 127 feet and the casing extended down to 103 feet. The second oil strata was found at a depth of 117 feet extending downward 5 feet or to a depth of 122 feet. The yield of oil at this depth was practically the same as that of the first strata, but a satisfactory pumping test could not be carried out with the mud bailer, there being no other appliance at hand.

It is believed that the strata, "the crumbling nature" of which made it necessary to case out the oil from the upper horizon, were principally shale, and probably represent the Bacau stage of the Vigo shale. Mr. McDaniel has stated in conversation that both the zones from which oil was obtained are sandy. Probably the shale above and below the "oil sands" was petroliferous throughout. Occasional sandy beds have been noted in the petroliferous shale, and it would be expected that where the conditions were such as to prevent its escape more oil would accumulate in the sandy beds than in the closer-grained shale.

If the wells are east of the anticlinal axis, as the relations indicate, the strata encountered probably dip at an angle of about $55°$. Well 1, consequently, pierces beds aggregating only 22 meters in thickness, and the upper and lower sandy zones are 0.87 meter and 1.04 meters thick, respectively.

In February, 1913, the well was pumped dry with the bailer. About 30 liters of oil were obtained from the column of water and oil which filled the casing to within 21 meters of the surface. The well proved to be 35 meters deep, the original casing having been driven to that depth recently. Apparently, the well is caved above the lower oil horizon reported, while the upper horizon is sealed off by the casing. It is probable that by proper treatment this well could be made to yield daily a barrel or so of oil.

Bahay well 2 is located 50 meters north of well 1 on the west bank of Bahay River. If the assumed structural relations are correct, well 2 is about 25 meters farther east of the anticlinal axis than well 1. Well 2 was drilled with a standard rig by Mr. O. A. Leary, and reached a depth of 91.5 meters. The casing at the collar of the well is 10 inches in diameter. Mr. Leary has kindly furnished the following statement which constitutes the only information available concerning this well:

Log of Bahay oil well 2.

0 to 25 feet.

    Conglomerate, yellow sand, clay and gravel with large bowlders.

25 to 100 feet.

    Brown shale showing evidences of oil and gas.

100 to 105 feet.

Coarse gravel with considerable quantity of oil and gas, and at this depth pipe was roughly packed and one-half-inch connection inserted. The gas was ignited and allowed to burn for fourteen hours without showing any decrease in volume, the blaze being approximately 10 feet in length.

105 to 115 feet.

Very hard gray rock; experienced considerable difficulty in drilling, owing to hardness.

115 to 170 feet.

Blue clay, showing streaks of clay lighter in color.

170 to 225 feet.

Brown shale heavily saturated with oil.

225 to 300 feet.

Brown shale very compact and of an elastic sticky nature. Drilling very difficult owing to this feature.

Very little water was encountered during the entire drilling of this well. At 20 feet a slight showing of fresh water; at 100 to 105 feet the presence of a small quantity of salt water was noticed. The well was practically free from water. Temperature of formation, normal.

Below the surface débris, which extends to a depth of 25 feet (7.6 meters), this well appears to have entered the Bacau stage of the Vigo shale and to have continued in this formation throughout. However, it may be that the "coarse gravel" and "hard gray rock" encountered in the well represent the conglomerate or gravel and the limestone exposed in Bahay River section (Table X, page 320) above the Vigo shale. The "evidence of oil and gas" in the "brown shale" above the "coarse gravel" is not in accord with this possibility, however, since the gray clayey sandstone exposed in Bahay River section above the conglomerate certainly shows no trace of oil or gas.

If the eastward dip of 55° in the shale north of the wells prevails at the site of well 2, the total thickness of strata pierced is 52.2 meters, the "coarse gravel" is 0.9 meter thick, and the "hard gray rock" is 1.9 meters thick.

PETROLEUM ON MILIPILIJUAN CREEK

Near the head of Milipilijuan Creek, which flows into Bahay River from the north, oil is encountered seeping directly from bluish to brownish black shale. The seep is at an elevation of 85 meters, and is approximately 1,500 meters north-northwest of the junction of Milipilijuan Creek and Bahay River. The shale from which the oil escapes dips northeast at an angle of 53° and contains some interbedded sandstone. Downstream a short distance, similar shale outcrops at several places, striking

northwest and dipping steeply both to the northeast and southwest.   Farther downstream the Canguinsa sandstone—massive and clayey—appears on top of the bedded shale.   The oil comes, therefore, from the usual petroliferous horizon in the Vigo shale, immediately beneath the Canguinsa sandstone.   The seepage is sufficient to permit of the collection of a liter of oil without much difficulty.

<div align="center">PETROLEUM ON SILI CREEK</div>

A large exposure of petroliferous shale occurs on Sili Creek, about 2 kilometers south of Tala.   The outcrop is at the confluence of two small streams which constitute the headwaters of Sili Creek, and is at an elevation of 100 meters.   The shale, which probably represents the Bacau stage of the Vigo shale, is exposed in banks about 12 meters high along either side of both branches of the creek for a distance of 100 meters.   Overlying the shale, the Canguinsa and Malumbang formations are exposed in the surrounding hills.   The structure in this region is not clear, but it appears that the exposure lies near the crest of a small anticline, trending north.   Faint bedding planes dipping to the east-northeast at angles of from 30° to 40° may be discerned in the shale.   No actual seepage of petroleum was observed, but the streams which flow across the shale are small and afford little chance for detecting films or seepage.   The odor of light oils is very strong in the neighborhood, and traces of oil can be obtained by macerating the shale in water.

Part of the shale outcrop at Sili is always barren of vegetation, a condition due, in part at least, to the instability of the surface which is constantly crumbling and sliding down into the streams. The natives attribute the absence of the generally present cogon to the petroleum in the shale.   They maintain that the shale has been known "to burn."   Two similar barren places occur in the vicinity of Bondoc Head.   The latter places are held by the natives to mark the graves of *asuan* (spirits).   The ground is said always to be hot and to have "burned with flames" in the past.   The reports of prospectors who had heard this story from the natives, but probably had not visited the site of the alleged phenomena, undoubtedly gave rise to the widely circulated statement that a vent, from which natural gas escaped and was continuously burning, existed near Bondoc Head.

The "graves of the asuan" are on Lomboy Creek above a village called Dyap, in a region covered with cogon.   Unlike the exposures on Sili Creek they are not steep slopes, but are on

fairly level ground.   Each has an area of several square meters which is barren of vegetation.   The ground to a depth of a meter, at least, below the surface is unusually warm and feels hot to the hands.   The temperature is not so high at the surface as it is at a depth of 30 centimeters, where the ground has a moldy, charred appearance and emits a rancid odor.

The sandy strata on which these bare spots occur are decidedly carbonaceous, and the surface is covered with decaying vegetable matter.   It appears that a slow oxidation of the carbonaceous material in the sandy beds and of plant remains on the surface is in progress locally in this vicinity.   The combustion may have been started originally by the fires which burn off the surrounding grass periodically.   While the sandstone and shale near Bondoc Head are strongly carbonaceous, they show little evidence of oil or gas.

PETROLEUM AT BACAU

Petroleum at Bacau appears as films or small globules on the surface of a pool in Canguinsa River at the foot of a steep bank of massive, blue-black shale.   The oil comes up intermittently from several places at the bottom of the pool, in quantity about equal to that encountered at Banco.   The seeps are at an elevation of about 100 meters.   The shale in the adjacent bank is petroliferous, and when fresh pieces are raked down into the stream they give off a film of oil.   The strata dip to the east at angles of from 50° to 60°, and apparently lie in the eastern limb near the axis of the Central anticline.   The Canguinsa sandstone occurs in the walls of the valley on either side immediately above the petroliferous shale, which is the type exposure of the Bacau stage of the Vigo shale.

PETROLEUM ON MALIPA CREEK

Inflammable gas bubbles up continuously from the bottom of Malipa Creek about 800 meters above the confluence of this stream and Vigo River.   Small films of oil are observed occasionally on the surface of the water in the vicinity.   The gas seeps from the Vigo shale in the south limb of the Malipa anticline.   A thickness of approximately 550 meters of shale is indicated by the outcrops between the horizon from which the gas comes and the axis of the anticline, while 250 meters of shale lie stratigraphically above the seep and below the Canguinsa sandstone.

A sample of the gas collected and analyzed by the Bureau of Science showed the following composition.

Table XIV.—*Composition of the gas from a gas seep on Malipa Creek.*

Constituent.	Per cent by volume.
Hydrogen	0.7
Methane	62.3
Ethane	0.3
Carbon dioxide	2.3
Nitrogen	25.5
Oxygen	7.2
Carbon monoxide	2.0

It will be noted that the gas contains an unusually large percentage of oxygen. Some of the oxygen may be due to contamination of the sample by air, although care was exercised to prevent contamination. Not all the oxygen can be due to the admixture of air, however, because the gas does not contain the corresponding proportion of nitrogen. It is probable, therefore, that the oxygen is an original constituent of the gas.

Mr. E. J. Cooke, in 1906, drilled a well on the west bank of Malipa Creek about 50 meters upstream from the gas vent. This well is said to have reached a depth of 21 meters and to have encountered a small quantity of oil. The top of the well is at an elevation of 20 meters.

PETROLEUM ON TANGOB CREEK

Inflammable gas and traces of petroleum can be obtained on the upper part of Tangob Creek by moving the stones and débris which cover the Vigo shale in the bed of the creek. In this vicinity Tangob Creek flows between Cambagaco Ridge on the east and a hill of volcanic agglomerate on the west. The outcrop of agglomerate is surrounded by Vigo shale, and the gas and oil are encountered within a few meters of the igneous rock. In the base of Cambagaco Ridge, Canguinsa sandstone occurs, overlying the shale and dipping to the east-northeast at an angle of about 20°. The lower part of the Canguinsa is rich in fossils where Tangob Creek flows across it. The shale at the point where the oil was observed is blue to black, and occurs in thin beds dipping east-northeast at an angle of 65°. The dip and strike of the shale are not constant, however, but vary greatly in this region. The petroleum seep is about in line with the axis of the Bato anticline, but the strata in which it occurs are part of the confused structure in the eastern limb of the Central anticline north of the Cabongahan.

PETROLEUM AT BATO

Petroleum has been found on the little creek just east of Bato in the shale forming the western limb of the acute fold described

as the Bato anticline. This locality is about 120 meters above sea level. There is no visible seepage, but petroleum may be obtained by digging into the banks of petroliferous shale along the stream. The strata belong to the Bacau stage of the Vigo shale.

PETROLEUM ON AJUS RIVER

At a point on Ajus River above the village of Ajus and about 4 kilometers from the mouth of the river, bubbles of inflammable gas and traces of petroleum appear on the surface of the water after a pole has been forced into the mud on the bottom. The oil occurs in the Vigo shale which dips steeply to the east and appears to be part of an overturned fold. The shale is bedded and petroliferous; layers of sandstone are interbedded in it, one of which, outcropping near the oil seep, is also slightly petroliferous. The elevation at the oil seep is about 45 meters.

PHYSICAL AND CHEMICAL PROPERTIES OF THE PETROLEUM

The petroleum encountered in the Tayabas field has a paraffin base, is low in specific gravity (36° to 39° Baume), and unusually mobile. It is light brown to wine-red by transmitted light, pale blue by reflected light. Different seeps afford petroleums which appear to be similar in character, although anaylses are available on the oil from only one source; namely, Bahay well 1 on Bahay River. Distillation yields a remarkably high proportion of gasoline, and the crude oil has an odor distinctly suggestive of light oils. George F. Richmond,[18] formerly of the Bureau of Science, made the earliest analyses of Tayabas petroleum, and later analyses have only confirmed his results. Richmond first tested a sample submitted by a commercial firm; and later, because the percentage of light distillates was so high as to arouse a suspicion that the sample was not authentic, he verified his findings upon samples collected at the well by Dr. George I. Adams, formerly of the Bureau of Science. Samples taken from the same well during the field work for this report were examined in the division of organic chemistry, Bureau of Science. The following table gives Richmond's analyses and other analyses of Tayabas petroleum made upon samples collected recently. For comparison, analyses of petroleums from neighboring islands and of well-known petroleums from other parts of the world are inserted.

[18] *Loc. cit.*

TABLE XV.—*Physical and chemical properties of petroleum from Bondoc Peninsula, Tayabas, from neighboring islands, and from important fields elsewhere.*

Description of petroleum.	References.	Crude oil.		Distillation products.							Remarks.
		Color by transmitted light.	Specific gravity.	Gasoline, to 150° C.		Kerosene, 150–300°C.		Heavy oils, 300–400° C.		Residue above 400° C.	
				Volume.	Specific gravity.	Volume.	Specific gravity.	Volume.	Specific gravity.		
Tayabas, Bahay well 1, depth 40 meters:				*Per cent.*		*Per cent.*		*Per cent.*		*Per cent.*	
1. Sampled by Castle Bros.-Wolf & Sons, Manila.	1	Brown to wine red.	0.826	39.0	0.756	47.1	0.882	13.9		2.0	Specific gravity at 15° C.
2. Sampled by division of mines, well not recently pumped.	1	...do...	.845	27.0		56.8		16.2			Do.
3.	2	...do...	a.8823	30.4	b.7692	50.9	c.8333	15.1	b.9961	3.6	Sulphur absent. Viscosity 61.5 seconds at 32°C. (Engler apparatus.)
4. Sampled by division of mines 24 hours after well had been drained.	1	...do...	.8325	39.0	.770	44.5	.850	16.5			Flash point 0° C. (32° F.). Sulphur absent. Initial boiling point, 91° C. Paraffin, 8.1 per cent. Specific gravity at 15°C.
Cebu, Philippines:											
1. Well at Toledo, Cebu.	3	Dark brown	.885	6.2	.762	42.32	.882	38.3	.901	13.17	Residue above 375° C. Specific gravity at 15°C.
2. Oil seep at Algeria, Cebu.	4	...do...		17.5		30.5		35.0			Residue contained foreign sediment.
3.	5	...do...	.842	13.5		37.5		31.5		2.9	Residue, coke.

	Ref	Color									Remarks
4.	[5]	---do---	.809	12.6		34.5		46.8			Flash point 12° C. (54° F.).
5.	[5]	---do---	.838	18.4		29.6		47.2		3.1	Flash point 27° C. (80° F.).
6.	[5]	---do---	.819								Residue, coke.
Leyte, Philippines	[5]		.926								Flash point 74° C. (166° F.).
Sumatra: 1.	[5]	Reddish brown	.833	19.7		46.9		31.1		.8	Residue, coke.
2.	[5]	---do---	.813	30.4		51.7		11.2		1.7	Do.
Java	[5]	Dark brown	.844	1.5		56.6		41.1		1.4	Do.
Borneo: Sarawak	[5]	---do---	.924	17.4				94.3		3.3	Do.
Kutei	[5]	---do---	.859	21.8		46.0		33.3		1.3	Do.
Japan: Echigo	[6]		.862			38.8		39.9			Paraffin. Mabery.
United States: California (Coalinga)	[7]		.9243	2.8	.7677	40.1	.867	38.1	.921	10.1	6.98 per cent paraffin.
Oklahoma (Glenn Pool)	[8]	Black	.8459	8.5	.7566	42.0	.8001	49.9	.9032		
Pennsylvania, Bradford.	[5]		.810	20.0		50.0		23.3		1.12	Residue, coke.
Russia: Grosny	[6]		.869	13.4	.730	25.6	.809	60.9			
Roumania: Campina	[6]		.824	37.7	.729	30.5	.823	31.8			Edeleanau.

[a] At 29° C.   [b] At 30° C.   [c] At 28° C.

1. C. F. Richmond, *loc cit.*
2. Division of organic chemistry, Bureau of Science, E. R. Dovey, analyst.
3. Division of organic chemistry, Bureau of Science, H. C. Brill, analyst.
4. Division of organic chemistry, Bureau of Science, D. S. Pratt, analyst.
5. Sir Boverton Redwood, Petroleum and its Products (1906), 7 2d ed., 216.
6. A. Beeby Thompson, Petroleum Mining (1910), 139.
7. T. C. Allen, Bulletin 398 U. S. G. S. (1910), 264.
8. David T. Day, *loc cit.*

A number of other samples said to represent Tayabas petroleum have been submitted to the Bureau of Science. One sample with the characteristic appearance of the Tayabas product, collected by Mr. E. J. Cooke, shows a specific gravity as low as 0.805. This sample probably came from the well on Malipa Creek.

Tayabas petroleum is of lower specific gravity than other known Philippine oils, and the fraction distilled below 150° C. is large enough to make the petroleum remarkable, although by no means unprecedented among natural products. By composition, Tayabas petroleum is more nearly related to some of the Sumatra oils than to those encountered in Cebu or Borneo. The lighter and most valuable grade of Japanese petroleum, that which is encountered in the lower productive horizons, is similar in character to Tayabas petroleum.

In studying sample 4, from Bahay well 1, Richmond found that 30 per cent of the crude oil, 16 per cent of the gasoline fraction, and 24 per cent of the kerosene fraction consisted of unsaturated hydrocarbons. Upon fractional distillation, the unsaturated hydrocarbons extracted from the crude oil began to boil at 130° C., and 7.5 per cent remained undistilled at a temperature of 300° C. The derivatives from the fractions showed a homologous series of aromatic hydrocarbons beginning with xylene (C_8H_{10}). Benzene, tuolene, nor any of the naphthalene series were found in them.

Mr. E. R. Dovey of the Bureau of Science examined sample 3 for optical activity. His results appear in Table XVI.

TABLE XVI.—*Optical properties of Tayabas petroleum. Sample No. 3.*

	Specific gravity at 29° C.	Refractive index at 29° C.	Optical rotation 29° C. (200-millimeter).
			Degrees.
Crude petroleum _____	0.8323	1.4639	_____
Gasoline fraction _____	.7692	1.4263	—0.55
Kerosene fraction _____	.8333	1.4670	— .11

ORIGIN AND PROBABLE QUANTITY OF THE PETROLEUM

Before discussing the particular features of this field having to do with the question of the origin of petroleum a few words should be devoted to the subject in general.

At present there are two sharply divided schools, in one of which the majority of geologists are to be found maintaining

that petroleum is of organic origin. In the other school are those who believe in the inorganic origin of petroleum, some of whom assert that there is a close relation between volcanic activity and the production of the natural hydrocarbons. It is only fair to admit, that the matter is by no means settled and that there is much which seems to support the inorganic theory.

The conditions of vulcanism under which petroleum is supposed to originate are still obscure, and it is impossible to say what kind of volcanic activity gives rise to petroleum. Coste,[19] the principal adherent of the volcanic theory, believes that the origin of oil is associated with solfataric emanations. If this be so, there are numerous localities in the Philippines where it might be advantageous to prospect. In the Tayabas field, however, where more oil is encountered than anywhere else in the Archipelago, the phenomena of vulcanism are least abundant and solfataric activity is unknown.

The observed facts bearing upon the question of the source of oil in this field are:

1. The formations are practically all sedimentary. Small isolated patches of volcanic agglomerate occur, but these are confined to the northeastern portion of the field and aside from the presence of this agglomerate there is no evidence of volcanic phenomena.

2. The known oil seeps are associated with bluish to brownish black shale and subordinate sandstone which occurs in the Bacau stage of the Vigo shale. Where traces of oil are found below the Bacau stage, they are always associated with beds of fine-grained compact shale. Material of this character occurs in other formations above the Vigo shale, but no petroleum has been observed in the upper formations.

3. In the petroliferous shale are numerous tests of *Globigerina* (Plate V) and some minute fragments of carbonaceous matter.

4. *Globigerina* has not been noted except in the Vigo shale. They were found most abundantly in the Bacau stage, but occur also at lower horizons.

5. None of the oil seeps in Tayabas appears to give off a large quantity of petroleum. However, all trace of the oil which is seen to be given off disappears in a remarkably short time, due probably to the light nature of the oil. Hence, it is possible that the quantity of oil which escapes from the seeps is larger than it appears to be.

6. Natural sections afford opportunity for the examination

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[19] *Trans. Am. Inst. Min. Eng.* (1906), **35**, 288.

of all the strata above the Vigo shale. The lower part of this formation and the beds which underlie it are not exposed anywhere within the field, and their character is unknown. There is a possibility also that some members of the Vigo shale above the Bacau stage are concealed by the overlap of the unconformable Canguinsa sandstone and, therefore, have escaped examination.

7. The petroleum is of low specific gravity, and contains a large proportion of light oils. It has been suggested that its properties are those of a clarified, or partly refined, oil. The lighter fractions are weakly levorotatory in their effect on polarized light.

Considering the field relations alone, the logical conclusion would be that the petroleum in Tayabas is of organic origin and is in no way connected with volcanic activity or other inorganic processes. By some authorities,[20] the property of rotating the plane of polarized light which Tayabas petroleum exhibits would be accepted as conclusive evidence of organic origin.

If a definite organic source is sought, the presence of *Globigerina* and vegetable remains in the Vigo shale at once attracts attention. Most of the oil observed occurs in the shale which contains organic matter of this nature, and it is well known that the decomposition, under certain conditions, of animal matter similar to the soft parts of *Globigerina* does give rise to petroleum.

The decomposition of organic matter, both *Globigerina* and vegetable remains, in the Bacau stage of the Vigo shale may have yielded the petroleum which is found in these beds. However, neither *Globigerina* nor the vegetable remains are especially abundant in the petroliferous beds, and it may be questioned whether the quantity of organic matter which was contained in the Bacau stage was adequate to have supplied a large quantity of petroleum, or even the quantity of petroleum which is to be observed.

Some of the properties of the Tayabas petroleum suggest that the oil may have migrated to its present position. Most oils obtained directly from the rocks in which it is certain that they have originated are high in specific gravity, and consist largely of heavy oils, with a very small gasoline content. On the other hand, oils which are believed to have migrated from a distant source, to the natural reservoirs in which they have accumulated, are of low specific gravity and are rich in volatile constituents.

[20] Engler, C., *Chem. Zentralbl.* (1908), 2, 376.

The refining or fractionation of petroleum by diffusion through porous media is well known, and the characteristic clarified or refined appearance of Tayabas oil might be so explained. It has been shown [21] experimentally that the diffusion of petroleum through porous media exercises also a selective function by which the unsaturated hydrocarbons are removed. The Tayabas petroleum has a moderately high content (30 per cent) of unsaturated hydrocarbons, the presence of which would seem to dispute the theory that the petroleum had been subjected to the refining effect of diffusion. However, a discussion of the origin of the petroleum in the oil fields of Kansas [22] quotes Dr. David T. Day in an expression of the belief that the Kansas petroleum shows the effects of diffusion, while according to the same authority [23] Kansas petroleums contain from 12 to 50 per cent of unsaturated hydrocarbons. Apparently, therefore, the presence of unsaturated hydrocarbons in the Tayabas oil is not incompatible with the theory that the oil has been refined by diffusion.

If the Tayabas petroleum has been refined by diffusion, the diffusion may have been either a lateral migration through the Bacau stage or a migration upward or downward from the neighboring strata. The formations exposed at the surface above the Bacau stage show no indication of oil. If the oil was ever present in these beds, the greater part of it must have escaped from their truncated edges along the anticlines. The Canguinsa sandstone is locally of such fine-grained and compact texture that it should retain traces of petroleum just as the shale in the Bacau stage does, if petroleum had originated in, or moved through, it. Apparently there is little chance that petroleum occurs in the formations above the Vigo shale.

It is possible that concealed members of the Vigo shale beneath the overlapping Canguinsa sandstone are petroliferous, and that petroleum from them migrates along the unconformity to the Bacau stage, which often appears at the surface immediately below the Canguinsa sandstone. If the petroleum were coming to the Bacau stage along the unconformity, it would be expected that the base of the Canguinsa sandstone would be most strongly petroliferous. This is not the case; usually, the petroleum appears in the beds of the Bacau stage and not along the unconformity. Moreover, in some places the Canguinsa sandstone

[21] Gilpin, J. E., and Cram, M. P., *Bull. U. S. Geol. Surv.* (1908), 365.
[22] Univ. Geol. Surv. of Kansas (1908), 9, 191.
[23] Day, David T., *Bull. U. S. Geol. Surv.* (1908), 381, pt. 2, 22.

has been removed by erosion so as to expose sandstone belonging to the Vigo shale above the Bacau stage, and this sandstone generally has not been found to be petroliferous. Thus, while the overlap of the Canguinsa sandstone may conceal petroliferous horizons, there is little direct evidence that these concealed horizons supply the petroleum which appears in the Bacau stage of the Vigo shale.

Similarly, there is a chance that the unexposed basal portion of the Vigo shale or a separate underlying formation is the source of petroleum which has moved upward through cracks and joints in the intervening beds to the Bacau stage. However, a relatively great thickness of strata is exposed in the limbs of the Central anticline between the Bacau stage and the lowest beds of the Vigo which have been uncovered by erosion, and there is but little evidence of oil in these intervening strata. Fresh surfaces in the occasional fine-grained beds only show traces of oil. Petroleum passing upward to the Bacau stage from a reservoir in the hidden lower part of the Vigo might be expected to leave traces along the outcrops of its passage through the intermediate rocks. From the fact that the petroliferous shale in the Bacau stage loses all evidence of oil after a short period of exposure, it might be argued that the relatively coarse sandy shales and sandstones between the Bacau stage and the lowest exposed part of the Vigo shale would retain no oil at the surface. In the data at hand, however, there is little evidence that the petroleum in the Bacau stage came there by diffusion from the base of the Vigo shale or from an underlying formation.

It appears, therefore, that while other accumulations of petroleum may exist in the concealed members of the Vigo shale, the petroleum in the Bacau stage probably originated somewhere in that stage, although it may have migrated laterally through the beds to the points at which it is now found.

If exploration proves that no oil exists in this field, except that which is evident in the Bacau stage of the Vigo shale, the possible production of petroleum will be confined to the area over which the strata are intact below the Canguinsa sandstone. The oil content of the petroliferous shale in the Bacau stage is probably low. Distillation of a sample, taken from a surface outcrop and kept in a sealed package before testing, yielded less than 1 per cent of oil. Beneath the surface where there has been no chance for volatilization to take place the proportion of oil is probably greater, but must still be relatively small because of the close-grained nature of the shale.

However, the petroliferous shale and interbedded sandstones make up the larger part of at least 50 meters thickness in some places, and probably approach this aggregate thickness on an average. Even with the low petroleum content specified, these beds would store up a volume of oil which assumes commercial proportions. Distributed throughout the shale, the oil could hardly be recovered in any quantity by ordinary methods, but if the saturation is great enough to cause an accumulation in the interbedded sandstones commercial exploitation should be possible. If the lenses of sandstone in the Bacau stage which are not exposed at the surface and consequently have not been broken open by erosion are saturated, the usual absence of oil in the sandstones along the outcrops of the petroliferous beds must be attributed to the rapid volatilization of the light oil from the surface of the porous materials.

The pore space in the interbedded sandstones is an important factor in this connection. Much of the coarser grained sandstone is so poorly consolidated that the actual pore space in the beds as they occur cannot be determined. A sample of the harder fine-grained sandstones taken from the vicinity of the Ajus petroleum seep contains 11 per cent of pore space. Probably the coarser sandstones are more porous.

Earlier examinations of Bondoc Peninsula have led to the published statement by two independent observers that the surface showing of oil is as favorable as those in other fields which have become large producers after development. It may now be added that the oil is associated with certain zones in an extensive series of shale and sandstone, and that the geologic structure is locally suitable for the accumulation of whatever petroleum is present.

A definite estimate of the quantity of petroleum available in this field, based solely on the data recorded in this report, in advance of any exploration is not justified. It would be a simple matter to estimate the thickness and area of the sands in the Bacau stage which could be reached by the drill in structurally favorable regions and to calculate the quantity of petroleum contained in these sands on the basis of their porosity as stated above, but the figure so obtained would have little real significance. The present knowledge of the field, however, does afford a basis for the belief that properly located wells could be made to yield at least small individual productions from the Bacau stage·of the Vigo shale. From the thinness of the sandstone beds and the alternation of sandstone and shale

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it may be concluded that the sandstone reservoirs are of small lateral extent and, consequently, that wells could be spaced closely without affecting each other. This being the case, the structurally favorable area over which the Bacau stage could be reached by drilling is large enough to make the total possible production of commercial importance. In addition to the possibilities of the Bacau stage there is the chance, which has been discussed, of obtaining oil at other horizons in the Vigo shale.

As evidence which bears somewhat on the question of obtaining petroleum on Bondoc Peninsula, it may be worth while to consider, briefly, the results of exploration for petroleum in other oriental fields. The general geology of the two important productive fields in the Orient, the Echigo field in Japan and the Moera Enim field in Sumatra, is similar to that of Bondoc Peninsula (compare Tables I, II, and III).

There are productive fields in Sarawak and in the eastern part of Borneo, but in British North Borneo the attempts to obtain petroleum have been unsuccessful. Although Borneo is adjacent to the Philippines, very little information is available concerning its economic geology and nothing is known of the geology of its petroleum resources.

In Formosa (Taiwan) which is also adjacent to the Philippines, only a small production, 6,200 barrels in 1908, [24] is recorded, although many shallow wells have been drilled. One of the few deep wells in the Byritsu Field on Formosa is said to yield a good flow of oil, and there is a possibility that with deeper drilling the Formosa petroleum fields will assume greater importance.

A well drilled in 1896 on Cebu Island in the Philippines, is said to have reached a depth of 300 meters; while it encountered considerable petroleum, it did not yield a satisfactory flow. The exploration was suspended before completion, because of the outbreak of an insurrection, and it has never been resumed. While the general geology of the two regions is similar, the local conditions at the site of the well in Cebu are different from those in Bondoc Peninsula. The drilling site at Toledo, Cebu, is located on the outcrop of the petroleum-bearing strata, and is within a few kilometers of the basal igneous complex upon the flank of which the beds lie, inclined at a high angle.

[24] Fukotome, K., Mineral Resources of Formosa (1910), 13. The Mineral Resources of the United States for 1911 reports 8,304 barrels of oil from Formosa in 1908 and 1,638 in 1911.

The foregoing brief statement includes practically all that is known concerning petroleum fields in the vicinity of the Philippine Archipelago.

AREAS TO BE PROSPECTED

Drilling on Bondoc Peninsula should be directed so as to answer three questions. It should determine (1) whether a sufficient quantity of oil is accumulated in the Bacau stage of the Vigo shale to afford a commercial production, (2) whether any members of the Vigo shale concealed by the overlap of the Canguinsa sandstone may be made to yield petroleum, and (3) whether there is petroleum in the unexposed base of the Vigo shale.

The same work should serve to determine points (1) and (2), since if wells are drilled through the Canguinsa sandstone to the Bacau stage of the Vigo shale on the limbs of the anticlines at varying distances from the axes, as is recommended later in this discussion, they will necessarily pass through any higher beds in the Vigo shale which may be covered unconformably by the Canguinsa sandstone.

If the Vigo shale is constant in the thickness which it displays in the Matataha River sections, it would not be feasible to explore both the Bacau stage and the basal portion of the Vigo shale with a single well, since the depth involved—even if the strata were horizontal—would approach 2,000 meters. It is possible that the Vigo shale is not of uniform thickness and that in some parts of the field a deep well might penetrate the entire series. Even so, however, wells from 400 to 600 meters in depth, located so as to pierce different horizons in the shale, would probably be less expensive and more suitable for initial exploration than a smaller number of very deep wells.

Without more data the anticlines in Bondoc Peninsula must be considered as the most favorable zones for exploration. The oil seeps are near the crests of anticlines generally and possibly in all cases. Experience in other oil fields has proved the theory of the accumulation of petroleum in anticlinal zones [25] to be of wide application. In the South Sumatra field and the Echigo field in Japan, which have been cited in comparison with the Bondoc field, production is reported to have come largely from the anticlines. In the former field only wells on the immediate crests of anticlines have been productive.

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[25] For a discussion of this theory consult *Bull. U. S. Geol. Surv.* (1907), **322**, 71 et seq.

In the local field a distinction must be made between those anticlines in which erosion has left the possible productive horizons intact across the arch and those in which erosion has proceeded along the crest until the oil-bearing strata have been cut through. Where the oil-bearing rocks are preserved across the anticline, oil—or gas—would be expected in the crest of the fold and wells should be located so as to explore the crest first. Where the productive beds are cut through along the crest and their edges exposed in the limbs of the anticline, the petroleum may be supposed to have escaped from outcrops along the axis and wells should be driven on the flanks of the fold in the hope of encountering a natural reservoir which does not appear at the surface and, consequently, has not been drained by seepage from its outcrop.

The anticlines in Bondoc Peninsula are generally asymetric; that is, one limb is steeper than the other. In drilling on an anticline of this character the limb with the lesser inclination affords better opportunity for exploration than the steeper limb. It is probably true, also, that the gentler limb of a sharp asymmetric anticline more generally has been found to be productive than the steeper limb.

The Maglihi anticline is probably the most suitable territory for the initial exploration of this field. The structure is favorable in that an anticlinal fold exists, although the anticline is more acute than would generally be considered desirable, and the petroleum-bearing strata are intact generally along its axis. The presence of petroleum in this anticline is established by the seeps at Banco, at Bahay, and on Milipilijuan Creek.

In the matter of the actual location of prospect wells, the factor of comparative accessibility will demand attention. The Maglihi anticline appears to be most favorable in structure near Mount Morabi. It would be desirable to have several test wells drilled through the crest and the western limb of the fold in this vicinity. The eastern limb should also be explored, but in it the strata dip very steeply, and the best location for the first wells would be difficult to determine exactly. The vicinity of Mount Morabi is relatively inaccessible as compared with Bahay farther north along the same flexure. The valley along the anticlinal crest near Mount Morabi is at least 250 meters above sea level, and the distance to the coast is about 6 kilometers.

At Bahay the anticline is not so clearly revealed as it is near Mount Morabi, and the structure may be less favorable, although the general conditions are similar. It would be feasible to

prospect the eastern limb of the anticline through the **Bacau** stage of the Vigo shale by two or three wells located at varying distances from the axis in the valley of Bahay River below the mouth of Milipilijuan Creek. Wells in this position would also pass through any members of the Vigo shale which may be concealed by the overlap of the Canguinsa sandstone. Similarly, the crest and the western limb could be explored by a line of wells up the valley of Apad Creek.

This general site is from 40 to 50 meters above sea level and from 4 to 5 kilometers from the coast. An old roadway, which might be utilized, leads into the region from the beach at the mouth of Bahay River.

Exploration of the limbs of the Maglihi anticline in the immediate vicinity of the oil seep on Bahay River or that on Milipilijuan Creek would involve more difficult transportation problems. Moreover, while the earliest drilling in many oil fields has been done in the vicinity of actual seeps, very often the larger production has developed in areas where oil seeps are not prominent. In exploration on Bondoc Peninsula it would be unwise to ignore the presence and distribution of the oil seeps, but it would be equally unwise to drill only where oil is to be seen.

The Central anticline should be explored by series of wells across its axis and both limbs adjacent to the axis in the vicinity of Bacau and, also, farther north near Balinsog. The structure is favorable at these places, and the presence of oil is established by the seep at Bacau. On account of its larger size, the Central anticline may contain larger accumulations of petroleum than would be expected in the Maglihi anticline. Bacau and Balinsog are each about 9 kilometers from the coast, and the intervening country reaches an elevation of 300 meters making these regions very inaccessible.

The Central anticline in the northern part of the field will afford valuable drilling territory if petroleum is found in the Vigo shale below the Bacau stage. On the other hand, if only the Bacau stage proves to be productive, the northern part of the Central anticline from which the Bacau stage has been removed by erosion loses its importance. South of Bacau the southerly plunge of the Central anticline probably carries the petroleum horizons down beyond the reach of the drill. Prospecting in the southern part of the peninsula in line with the Central anticline would determine this point and might prove successful.

The possible locations which have been discussed are all near oil seeps and are on sharp anticlinal folds. The Ayoni anti-

cline has no oil seep on its crest, and it is a broad gentle fold. The fact that no petroleum escapes from it may be taken as an unfavorable or a favorable indication, arguing either the absence of petroleum or that the petroleum has been confined by the unbroken strata, there having been no opportunity for it to reach the surface here, such as is afforded by the cracked and fissured axial portions of the sharper folds. A broad gentle anticline is generally looked upon with more favor as a natural reservoir for petroleum than an acute anticline. Judged by this standard, the Ayoni anticline would be considered promising. It is readily accessible, and there has been comparatively little erosion along its crest. Wells on its crest and eastern limb should pierce the upper part of the Vigo shale under favorable conditions.

On the other hand, there is an apparent transition in the character of the Vigo shale from east to west at this latitude by which shale grades into sandstone. It is possible that the shales which appear to be the principal oil-bearing rocks are less extensive in the vicinity of Ayoni than elsewhere. The absence of seepage, however, which might be taken to indicate such a change in the character of the formations, can be accounted for readily enough on other grounds as suggested above.

Wells should be drilled along Malipa Creek, in the southern limb of the Malipa anticline, and also, probably, farther south in the eastern limb of the Central anticline. The structure is not unfavorable, and traces of oil and gas are in evidence. A well near the axis of the Malipa anticline would reach the beds in the lower part of the Vigo shale, and from a site farther up the creek higher strata including the Bacau stage could be investigated. This region could be reached with comparative ease by coming up the valley of Vigo River from the coast.

The Bato anticline is not easily accessible, and the structural relations are not clearly enough defined to make it a favorable site for the first drilling, although it appears to be relatively good territory. The lower part of the western base of Cambagaco Ridge would be a favorable site for testing the beds in the Vigo shale beneath the overlap of the Canguinsa sandstone. Wells so located, if drilled deep enough, would also encounter the Bacau stage of the Vigo shale in fairly good structural relations.

To reach the base of the Vigo shale and determine the value of this zone in connection with petroleum, wells should start at the lowest possible stratigraphic horizon. The upper valley of Sibuyanin River in the western limb near the axis of the Central anticline is probably the best site for such wells. The beds at

the surface here appear to be about 1,400 meters, stratigraphically, below the base of the Canguinsa sandstone, and the dip is about 35°. The eastern limb just across the axis in the upper valley of Vigo River is equally desirable as a drilling site except for the steeper dip (from 60° to 70°) of the strata.

If oil is obtained in any of these localities, a number of places which have not been mentioned may become desirable territory, depending on what horizon the oil is encountered in and on other conditions which will be revealed by the drilling. More detailed work in the vicinities of Ajus and Sili may show that there are favorable drilling sites at these places, and as has been suggested the neighborhood of the volcanic agglomerate may prove valuable as drilling territory.

It will be apparent that companies entering this field should be prepared to drill several wells in order to prospect any locality thoroughly. The failure of a single drilling should not be accepted as establishing the absence of exploitable petroleum resources in any particular zone or in any one anticline, and certainly should not condemn the whole field. The drilling of unsuccessful wells is common in producing fields, where the geology is well known and the experience gained from many completed wells is available. It would be surprising, indeed, if the early drilling on Bondoc Peninsula did not result in a large proportion of "dry" wells, even if exploration were ultimately successful.

Skilled and experienced drillers should be secured. It is anticipated that drilling on Bondoc Peninsula will be rendered difficult by the unconsolidated, caving nature of the shale series, and, possibly, by the necessity of sealing off water-bearing sands. Because of the fact that these difficulties have been overcome successfully in the California oil fields, drillers from these fields should have experience that would be particularly valuable in the local field.

The exact location of wells should be preceded by further and more detailed geologic study of the region to be tested. The relation of possible sites to the known and suspected petroliferous zones should be carefully determined, and local variations or irregularities in the general structural and geologic features, as outlined in this report, should be noted before a decision is reached as to the best drilling site. The progress of the first drilling likewise should receive particularly close attention from a geological standpoint since it may reveal conditions not manifest at the surface which would alter the course of exploratory work.

CONCLUSIONS

The existence of petroleum on Bondoc Peninsula is established by the presence of seeps of petroleum associated with inflammable gas at various places throughout the oil field.

All the petroleum encountered so far is similar in character and of a good quality. It is of low specific gravity, and contains a large proportion of light oils which would make it of relatively high value as a commercial petroleum.

The seeps are in highly inclined strata which are probably in all cases part of the structure of anticlinal folds. From this association it is believed that the petroleum in this field has tended to collect in the crests of anticlines in accordance with the general law of petroleum accumulation.

The petroleum occurs associated with certain horizons in an extensive series of beds of sandstone and shale (Vigo shale), which is similar in character to the oil-bearing rocks of productive fields. The principal seeps are found in the upper part of this series in a zone designated as the Bacau stage, which is predominantly shale, but contains subordinate beds of sandstone. In its seepage, the petroleum is associated with the shale rather than the sandstone and may be observed in some cases to come directly from the shale, but this association may be due to the ready escape of the light oil from the outcrops of the coarse-grained beds and its retention at the surface in the fine-grained shale only.

The petroleum may have originated, in part at least, in the globigerina and other organic remains found in the strata with which the oil is associated. There is a possibility, however, that the oil is not indigenous to the strata in which it now occurs, but has migrated from its source in another horizon. Beds which are concealed so that they cannot be examined at the surface and which, consequently, may be sources of oil occur as follows: (1) Members of the Vigo shale above the Bacau stage, concealed by the overlap of the Canguinsa sandstone which overlies the Vigo shale unconformably; (2) the basal portion of the Vigo shale which has not been uncovered by erosion; and (3) any sedimentary formations which may underlie the Vigo shale.

The structure of Bondoc Peninsula includes a number of anticlinal folds, and the conditions along some of these anticlines are considered favorable for the accumulation and retention of the petroleum, whether it occurs in all or in any one of the horizons at which it is suspected.

Drilling exploration is recommended and should be conducted along lines which have been indicated. Wells should be so located as to explore the Bacau stage of the Vigo shale thoroughly under favorable conditions of structure. The possible sources of petroleum outside the Bacau stage likewise warrant exploration. Areas considered favorable for prospecting by test wells have been outlined.

The quantity of petroleum which might be recovered commercially from this field is undetermined. Certain geologic features which have been pointed out lead to the belief that only wells of small individual productions will be obtained; but it is also probable that wells of this character could be closely spaced without mutual interference and that the territory within which they could be located is large. A sufficient number of these wells, drilled in groups so as to be operated from local centers, might reasonably be expected to yield an aggregate quantity of limited commercial proportions. There is a possibility, conditioned largely upon the presence of oil at a horizon other than the Bacau stage of the Vigo shale, of obtaining wells of larger individual flow and a greater total production of petroleum.

ILLUSTRATIONS

PLATE I

Fossils from raised coral reefs (Recent and Pleistocene). About one-half natural size. (Photographs by Martin.)

FIG. 1. *Conus flavidus* Lam.
FIGS. 2 and 3. *Voluta* sp.
FIG. 4. *Potamides* sp.
5. *Spondylus* sp.
6. *Telescopium telescopium* Linn.
7. *Natica* sp.
8. *Trochus fenestratus* Gmel.

FIG. 9. *Crista pectinata* Linn.
10. *Cerithium nodulosum* Brug.
11. *Circe pectinata* Linn.
12. *Cerithium jenkinsi* K. Mart. (?)
13. *Arca cecillei* Phil. (?)
14. *Strombus canarium* Linn.

PLATE II

Fossils from the Upper limestone and the Cudiapi sandstone of the Malumbang series (Pliocene and upper or middle Miocene). About one-half natural size. (Photographs by Martin.)

FIG. 1. *Pecten senatorius* Gmel.
2. *Cytherea* sp.
3. *Lagenum multiforme* K. Mart. var. *tayabum* var. nov.
4. *Spondylus imperialis* Chem.
5. *Schizaster subrhomboidalis* Herkl.

FIG. 6. *Cyclolites* sp.
7. Indet.
8. *Turbo* sp.
9. *Cardium* sp.
10. *Conus* sp.

PLATE III

Fossils from the Lower limestone of the Malumbang series (upper or middle Miocene). About one-half natural size. (Photographs by Martin.)

FIG. 1. Indet.
2. *Cypraea* sp.
3. Portion of internal cast of *Cerithium* sp.

FIG. 4. *Schizaster subrhomboidalis* Herkl.
5. *Pyrula gigas* K. Mart.
6. *Macoma* sp.

PLATE IV

Fossils from the Canguinsa sandstone (middle or lower Miocene) and from the Vigo shale (lower Miocene or Oligocene). About one-half natural size. (Photographs by Martin.)

FIG. 1. *Conus loroisii* Kien.
2. *Conus ornatissimus* K. Mart.
3. *Pyrula bucephala* Lam. (?)
4. *Tapes rimosa* Phil.
5. *Corbula socialis* K. Mart.
6. *Conus djarianensis* K. Mart.

FIG. 7. Indet.
8. *Hindsia* sp.
9. *Arca* sp.
10. *Cyclolites* sp.
11. *Strombus triangulatus* K. Mart. (?)

PLATE V

Globigerina (Rhizopoda) from the Vigo shale; a possible source of petroleum. (Drawings by Moskaira.)

FIGS. 1 to 3. Characteristic shapes assumed. Magnification, 20 to 25 diameters.
4 and 5. Details of the structure of the shell. Magnification fig. 4, 20 to 25 diameters; fig. 5, 140 diameters.

PLATE VI

FIG. 1. Bahay well 2 on the property of the Bahay Valley Oil Company, Bahay. (Photograph by Pratt.)

2. Looking eastward near the mouth of Cambagnaon Creek. The hills in the distance lie on the eastern flank of the Central anticline. (Photograph by Manila Mining Association.)

PLATE VII

(Photographs by Manila Mining Association)

FIG. 1. Looking west-northwestward across Vigo River near the eastern coast of the peninsula; the eastern slope of Mount Dagmit to the left, and in the distance beyond the river, a part of Cambagaco Ridge with characteristic slope to the eastward resulting from the eastward dip of the strata.

2. The eastern wall of the upper valley of Canguinsa River south of Balinsog Hill.

PLATE VIII

(Photographs by Manila Mining Association)

FIG. 1. Looking northward from near Balinsog Hill.

2. Looking westward from near Balinsog Hill, across the upper valley of Canguinsa River, which marks the crest of the Central anticline, to Cudiapi Range on the western limb of the Central anticline; South Cudiapi Mountain in the middle distance.

PLATE IX

(Photographs by Pratt)

FIG. 1. Looking east-northeastward across the valley of Malipa Creek toward the ridge along the eastern coast, Mount Cambagaco to the left, gap formed by Vigo River in center, and Mount Dagmit to the right.

2. South Cudiapi Mountain across the valley of Bondoc River; looking northeastward from a point 2 kilometers south of Bondoc.

3. Mount Cancalao in the valley of Matataha River; looking westward.

PLATE X

(Photographs by Pratt)

FIG. 1. Outcrop of Cudiapi sandstone in the eastern limb of the Central anticline; looking northwestward from near the head of Canguinsa River.

2. Outcrop of Canguinsa sandstone in the eastern limb of the Maglihi anticline on the lower part of Bahay River; looking southward.

3. Nearly vertical Vigo shale near the axis of the Central anticline on the lower part of Cambagnaon Creek; looking southward.

4. Outcrop of volcanic agglomerate near Dumalog Creek.

MAP

Geologic reconnaissance map of a part of Bondoc Peninsula with 5 geologic sections.

TEXT FIGURE

FIG. 1. Diagrammatic section in the upper valley of Malipa Creek.
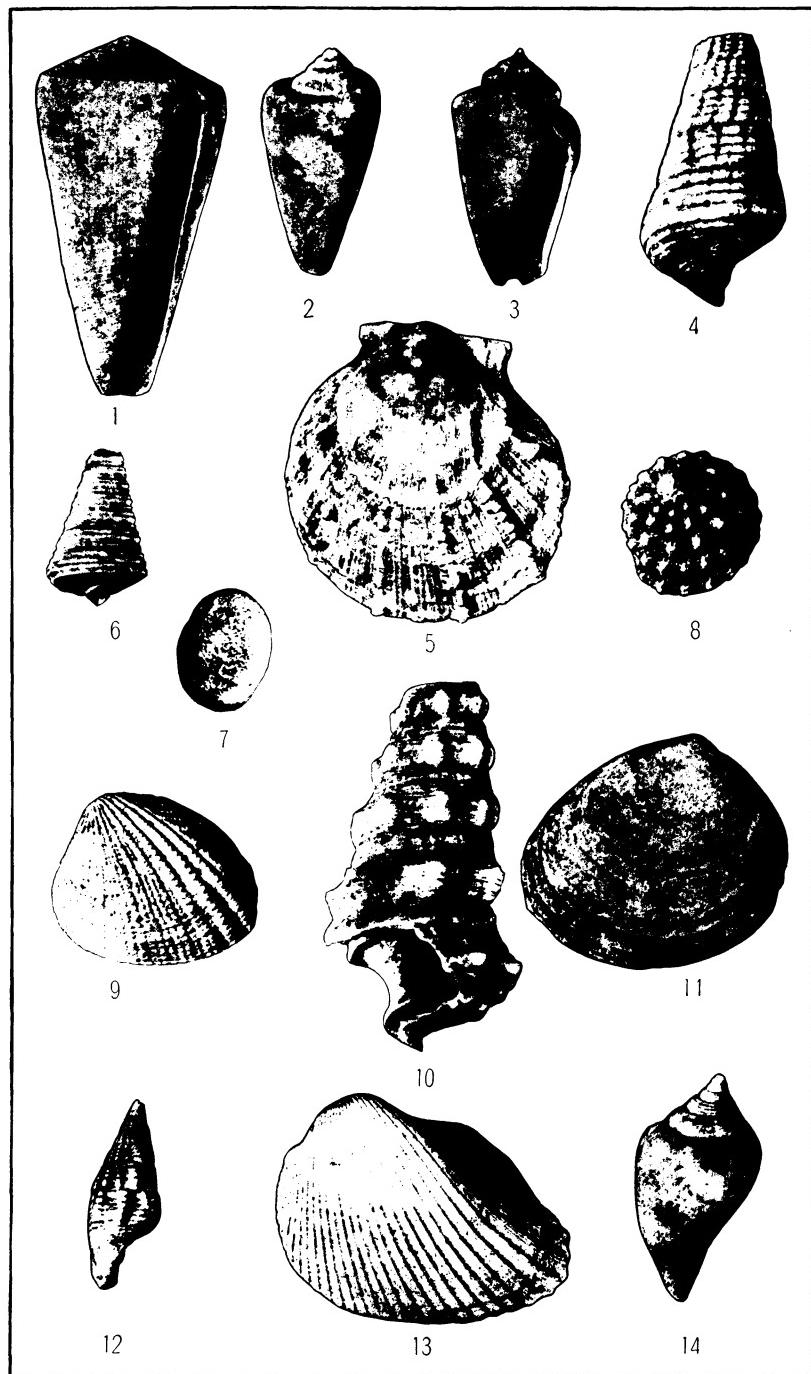
PLATE I.

Fossils from raised coral reefs (Recent and Pleistocene). Fig. 1. Conus flavidus Lam. 2, 3.
    Voluta sp. 4. Potamides sp. 5. Spondylus sp. 6. Telescopium telescopium Linn. 7. Natica
    sp. 8. Trochus fenestratus Gmel. 9. Crista pectinata Linn. 10. Cerithium nodulosum Brug.
    11. Circe pectinata Linn. 12. Cerithium jenkinsi K. Mart. (?) 13. Arca cecillei Phil. (?)
    14. Strombus canarium Linn. About one-half natural size.
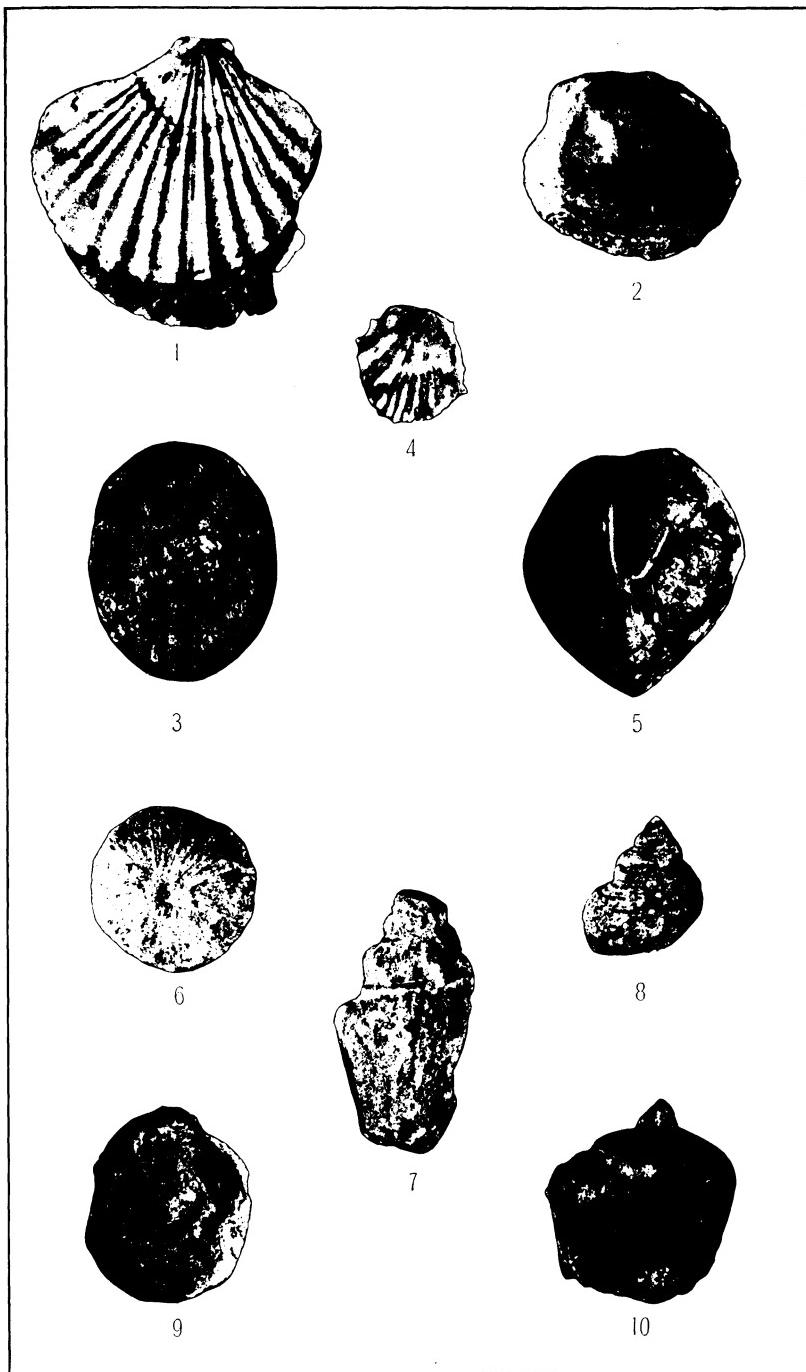
PLATE II.

Fossils from the Upper limestone and the Cudiapi sandstone of the Malumbang series (Pliocene and upper or middle Miocene). Fig. 1. Pecten senatorius Gmel. 2. Cytherea sp. 3. Lagenum multiforme K. Mart. var. tayabum var. nov. 4. Spondylus imperialis Chem. 5. Schizaster subrhomboidalis Herkl. 6. Cyclolites sp. 7. Indet. 8. Turbo sp. 9. Cardium sp. 10. Conus sp. About one-half natural size.
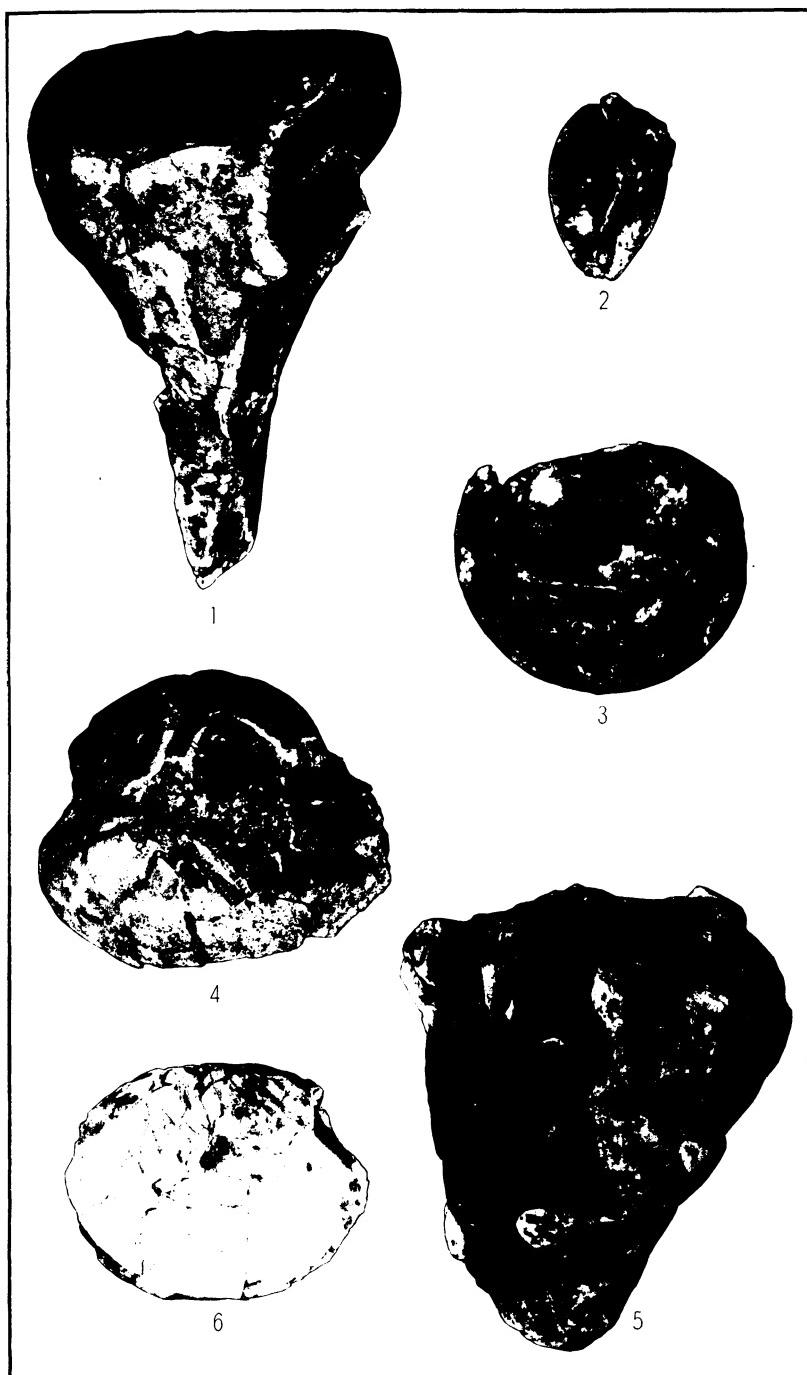
PLATE III.

Fossils from the Lower limestone of the Malumbang series (upper or middle Miocene). Fig. 1. Indet. 2. Cypraea sp. 3. Portion of internal cast of Cerithium sp. 4. Schizaster subrhom-boidalis Herkl. 5. Pyrula gigas K. Mart. 6. Macoma sp. About one-half natural size.
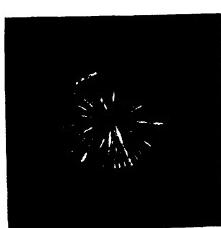
PLATE IV.

Fossils from the Canguinsa sandstone (middle or lower Miocene) and from the Vigo shale
    (lower Miocene or Oligocene).   Fig. 1. Conus loroisii Kien.   2. Conus ornatissimus K. Mart.
    3. Pyrula bucephala Lam. (?)   4. Tapes rimosa Phil.   5. Corbula socialis K. Mart.   6. Conus
    djarianensis K. Mart.   7. Indet.   8. Hindsia sp.   9. Arca sp.   10. Cyclolites sp.   11. Strombus
    triangulatus K. Mart. (?)   About one-half natural size.
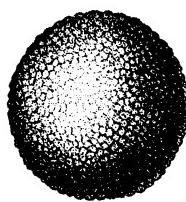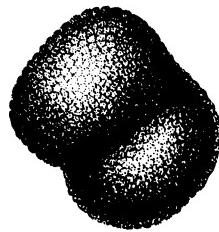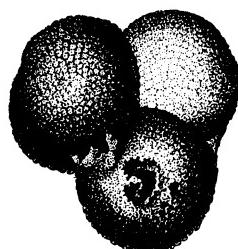
PLATE V.

Globigerina (Rhizopoda) from the Vigo shale; a possible source of petroleum.　Figs. 1–3. Characteristic shapes assumed.　4, 5. Details of the structure of the shell.

Fig. 1. Bahay well 2.
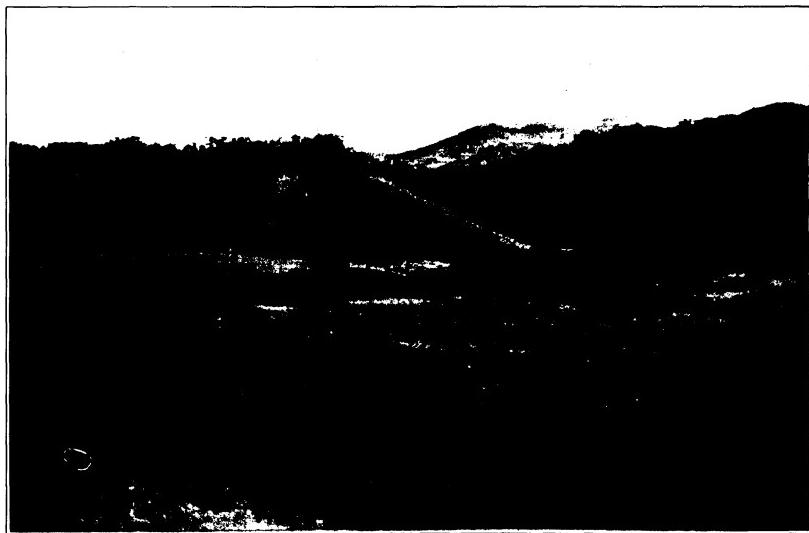
Fig. 2. Looking eastward near the mouth of Cambagnaon Creek.

PLATE VI.
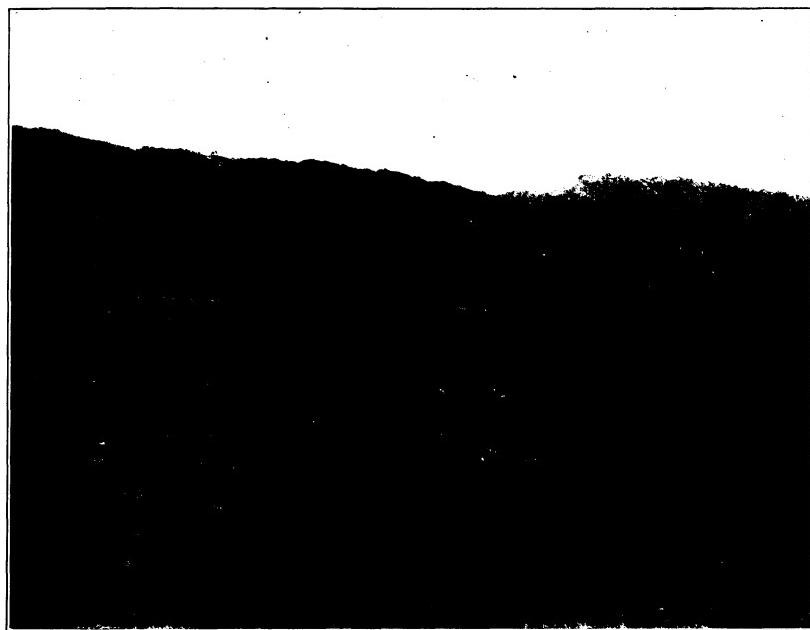
Fig. 1. Looking west-northwestward across Vigo River.

Fig. 2. The eastern wall of the upper valley of Canguinsa River.

PLATE VII.
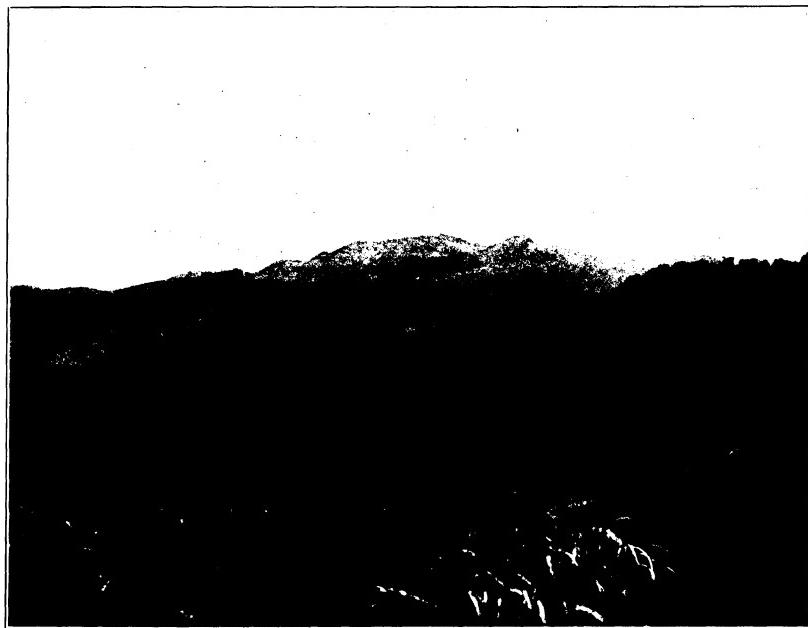
Fig. 1.   Looking northward from near Balinsog Hill.
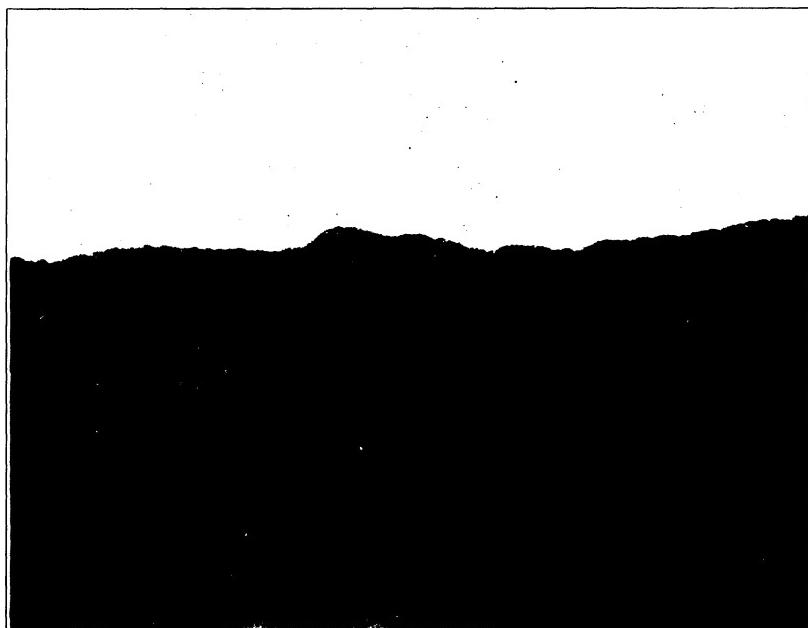
Fig. 2.   Looking westward from near Balinsog Hill.

PLATE VIII.
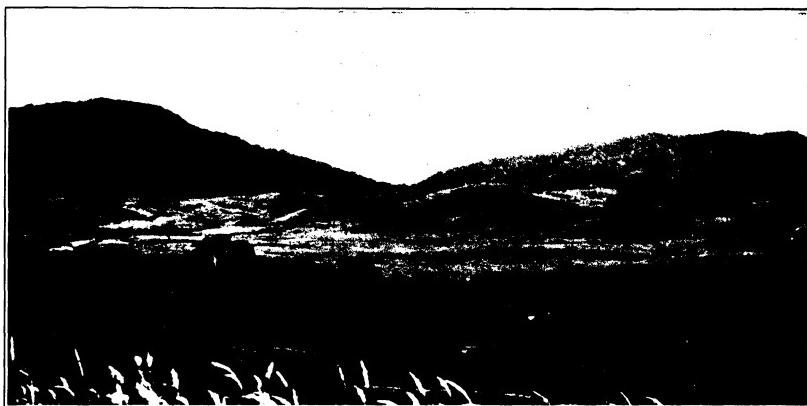
Fig. 1. Looking east-northeastward across the valley of Malipa Creek.
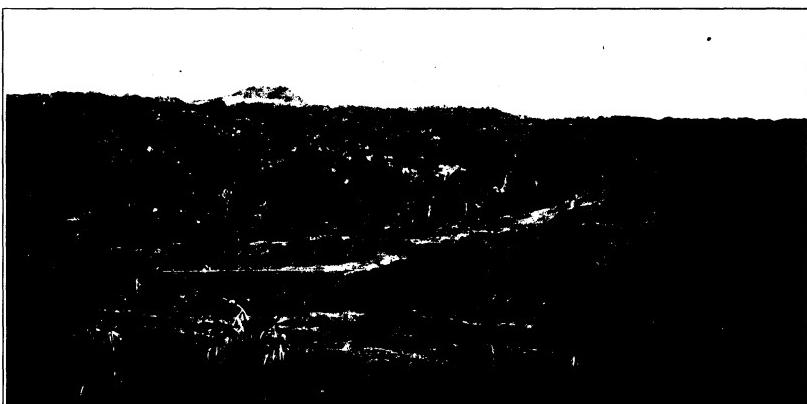
Fig. 2. South Cudiapi Mountain across the valley of Bondoc River, looking northeastward.
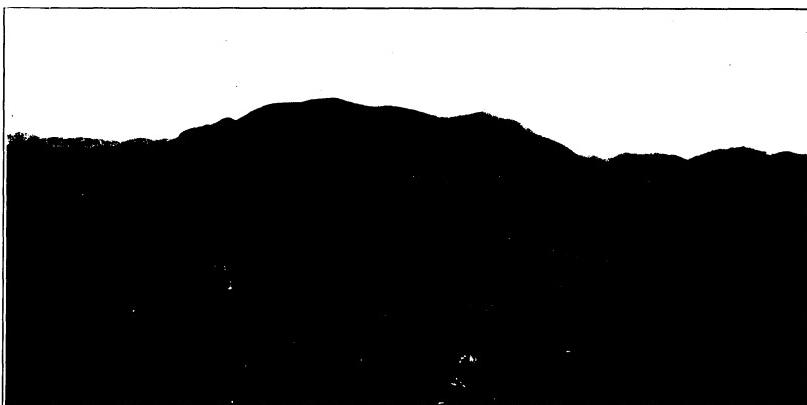
Fig. 3. Mount Cancalao, looking westward.

PLATE IX.
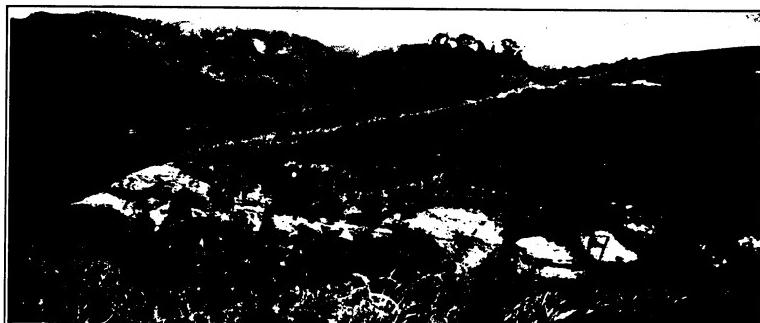
Fig. 1. An outcrop of Cudiapi sandstone.

Fig. 2. An outcrop of Canguinsa sandstone.

Fig. 3. Nearly vertical Vigo shale.

Fig. 4. An outcrop of volcanic agglomerate.

PLATE X.

Oversized
Foldout

THE NIPA PALM AS A COMMERCIAL SOURCE OF SUGAR

A CONSIDERATION OF THE PRINCIPAL DIFFICULTIES ENCOUNTERED IN COLLECTING AND PRESERVING NIPA-PALM SAP

By D. S. PRATT, L. W. THURLOW, R. R. WILLIAMS, and H. D. GIBBS [1]

(From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.)

The nipa palm, *Nipa fructicans* Wurmb., covers large areas of swamp land in various parts of the tropics. The requirements for its growth and proper development are few, consisting of low river land subject to periodic overflow by brackish tide water. Large areas of this character, covered almost exclusively with the nipa palm, exist in several provinces throughout the Philippine Islands. At the present time the sap exuded by the flower stalk when it is cut is utilized on a large scale as a commercial source of alcohol.

The manufacture of nipa alcohol and the distribution of the palm in the Islands have been investigated, and preliminary experiments by one of us [2] on the manufacture of sugar have

[1] Associate professor of Chemistry, University of the Philippines.— EDITOR.

[2] Gibbs, H. D., *This Journal*, Sec. A (1911), 6, 99–206. At that time experiments on a commercial scale seemed impossible for the reason that no modern sugar mill existed on Luzon. This difficulty was removed by the construction of a 10-ton mill at Muntinlupa, Rizal Province, 33 kilometers by railroad south of Manila. A description of this mill has been published in *This Journal*, Sec. A (1912), 7, 357, by Thurlow and Pratt.

been carried on. These results were eminently satisfactory, and lead directly to further study on a more extensive scale. Many other palms, such as the coconut, buri, and sugar palms, elaborate a sweet juice containing sucrose, and have been suggested as possible commercial sources of refined sugar. The nipa offers many distinct advantages not found with other palms. It is already extensively grown in localities that otherwise would remain waste land, but which offer cheap water transportation for juice from swamp to mill. The collection of sap is greatly facilitated by the nature of the palm, since it produces the flower stalk close to the surface of the ground and within easy reach. With other palms, such as the coconut and buri, the sap is gathered at a considerable elevation from the ground that necessitates climbing and increases the cost of collection.

The method utilized for many years in collecting the sugar-bearing nipa sap, or *tuba* as it is generally called, is to cut off the recently formed fruit at its point of attachment to the stalk. The sap flows freely from the freshly cut surface of the stalk, and is collected in bamboo joints called *tuquils* or *bombones*. These vary in size and shape, depending upon the customs of the natives working in variously located swamps. In the large areas of Bulacan Province, the tuquils are about 50 centimeters long, with a diameter of 10 centimeters and a capacity of from 1 to 2 liters, while those employed in other districts often exceed a meter in length and are capable of holding several liters of tuba. The receptacle has a small hole in the side wall near the upper extremity through which the stalk of the palm is introduced, serving to support the bombon and allow the sap to drop into the interior. The *tuberos*—men employed in gathering the sap—visit the palms twice a day, and cut off a thin slice from the end of the flower stalk to keep the wound fresh and prevent stoppage in the flow of sap.

It has been shown [3] that a stalk normally flows for about three months, during which time it produces from 30 to 50 liters of sap, the greater portion of which is secreted during the first two months after tapping. The yield of sap may be partially equalized by progressive tapping of new palms, but much depends upon the season.

The number of palms per hectare varies within wide limits, as might be expected, since many swamps have been used for years and have received at least a moderate amount of attention,

[3] Gibbs, *loc. cit.*

while other unworked areas are overgrown and choked. The former naturally support fewer palms of superior quality comprising a larger proportion of fruiting plants. A conservative estimate for cultivated *nipales,* or nipa swamps, may be placed at from 2,000 to 2,500 palms per hectare, of which 750 may be depended upon to produce fruiting stalks and consequently be available for sap collections. Proper attention in keeping the swamps free from overcrowding and intelligent care in selection would doubtless greatly increase the percentage of flowering plants, and might raise the average individual production of sap and its sucrose content.

THE CHARACTER OF THE SAP

The nipa sap collected in the above manner and transported to the distilleries is of no value for the manufacture of sugar. Many factors to be discussed later have resulted in causing more or less complete inversion of the sucrose followed by alcoholic and acidic fermentation. Nipa sap is very susceptible to changes of this character, any of which are fatal to its utilization as a source of refined sugar.

The sap as it flows from the cut surface of the flower stalk is water white, practically neutral, and possesses a characteristic odor. The composition varies considerably, depending upon the age of the flower stalk—or time that has elapsed since it was first cut—the season, the location, and the individuality of the palm. The tendency of nipa sap to undergo inversion within a few hours after collection, even when great care has been employed to obtain aseptic samples, and the impracticability of laboratory work in the swamp render it difficult to obtain as many analyses of fresh sap as could be desired. No preservatives have been found efficient in preventing change in the character of the juice without introducing a relatively large amount of foreign material. The only satisfactory method is to collect the sap directly in clean bottles and sterilize by heat within an hour or two after starting the collection.

The average nipa sap as it flows from the palm has approximately the following composition:

Density 15°/15°	1.0670
Brix	17.0
Apparent purity	90.0
Invert sugar	Trace.
Sucrose	15.0 per cent.
Nitrogen	0.049 per cent.
Ash	0.60 per cent.
Sodium chloride	0.45 per cent.

Toward the end of the period of flow, the percentage of sucrose and the purity decrease. Table I shows the sucrose content of nipa sap collected in Bulacan Province on September 15, 1912. The samples were collected in polariscope tubes hung on the palms and polarized directly. The per cent sucrose is calculated from the polarization, assuming an apparent purity of 90. The error thus introduced is slight, as shown by experience.

TABLE I.—*Per cent sucrose in various samples of nipa sap from 99 individual palms. Collected in the Bulacan region, September 15, 1912.*[a]

Sample No.	North of San Esteban.	Southeast of San Esteban.	Guagua.	South of San Esteban.	Consuelo.	Sapa Cauayan.	Hagonoy.
1	14.3	15.9	15.7	15.6	11.6	12.2	14.8
2	15.8	13.7	13.6	15.6	10.1	10.6	14.7
3	15.5	14.3	14.7	17.5	13.3	11.8	15.8
4	12.8	12.9	15.0	15.6	10.9	12.5	17.3
5	16.8	13.6	15.9	17.1	10.2	13.1	12.9
6	15.2	15.6	15.3	16.2	13.5	13.5	14.1
7	15.3	15.7	14.6	17.7	11.1	16.2	15.5
8	15.4	13.6	12.7	17.3	12.2	15.2	13.3
9	15.4	15.7	14.6	16.0	10.5	14.5	15.3
10		14.6	15.1	17.7	10.7	17.4	14.4
11		16.0		17.4	10.8	12.5	15.2
12		16.4		16.8	11.5		
13		16.9		16.5	11.2		
14		15.8		16.7	11.2		
15		14.1		17.8	13.9		
16		13.9		14.7	11.5		
17				16.8	8.4		
18				17.4	10.8		
19				17.1	11.9		
20				17.8	11.1		
21					12.2		
22					12.8		
Average	15.2	14.9	14.7	16.8	11.4	13.6	14.8

[a] Determinations by E. R. Dovey.

Table II shows the total sugar and volume of juice per twenty-four hours from 20 palms with flower stalks of various lengths. As the stalks are sliced daily when flowing, they become shorter as the season advances. These samples represent sap flowing near the end of an abnormal season during which lack of rain and other climatic conditions rendered the supply of tuba very scant and of poor quality.

TABLE II.—*Samples of nipa juice collected near Malolos, December 1, 1912.*

No.	Length of stalk.	Sucrose.	Volume of juice in 24 hours.	Sucrose in 24 hours.
	cm.	Per cent.	cc.	Grams.
1	30	10.1	420	42.4
2	60	12.4	380	47.2
8	50	11.6	500	58.0
4	55	9.7	730	70.8
5	35	12.4	620	76.8
6	37	12.6	630	79.4
7	70	13.3	590	78.5
8	100	12.9	940	121.1
9	65	12.0	510	61.3
10	60	15.3	380	58.2
11	63	13.1	460	60.3
12	110	11.3	470	53.3
13	90	14.8	510	75.4
14	65	14.2	320	45.5
15	70	11.8	450	53.3
16	60	13.0	480	62.4
17	70	13.1	540	70.7
18	50	12.8	550	70.5
19	60	12.6	530	66.8
20	70	11.5	740	85.0
Average		13.0	537	69.8

Table III shows the percentage of sucrose and purity of nipa juice collected near Malolos, Bulacan Province, on January 10, 1913. It is evident that the purity as well as sugar content of the sap has decreased to a considerable extent since the analyses given in Table I.

TABLE III.—*Samples collected near Malolos, January 10, 1913.*

No.	Length of stalk.	Brix.	Sucrose.	Purity.
	cm.		*Per cent.*	
1	75	10.7	7.7	72
2	60	11.7	9.4	81
3	60	10.5	8.5	81
4	75	11.7	10.0	85
5	90	11.7	9.4	81
6	105	12.6	10.5	83
7	75	12.9	10.5	81
8	75	13.1	11.3	87
9	100	13.8	11.9	86
10	105	13.6	11.0	81
11	45	14.3	11.5	80
12	30	12.9	10.6	82
13	25	12.6	10.4	83
14	30	13.8	11.1	80
15	15	14.7	11.7	80
16	15	14.3	11.7	82
17	20	12.9	10.8	84
18	60	16.8	13.4	80
19	15	16.6	13.3	80
20	25	15.0	12.2	82
Average		13.3	10.9	81.5

From the above tables and other analyses [4] it may be definitely stated that nipa sap as it issues from the palm is exceptionally well adapted to the manufacture of sugar. The acids, waxes, etc. of sugar-cane juice are absent, the sap is free from invert sugar, contains no débris, and is colorless. If it were possible to transport the tuba without deterioration due to inversion and fermentation to a mill, no difficulty would be experienced in producing white sugar.

DETERIORATION OF NIPA SAP

The inversion of sucrose and subsequent fermentation take place very rapidly after the sap drops into the bamboo tuquils. These are always exceedingly dirty, as no effort is made to remove the accumulation of slime and sediment adhering to the interior. It could not be expected under these conditions that a sucrose solution would long remain unchanged in a tropical climate. However, nipa sap begins to invert within about four hours after leaving the palm, even when collected in sterile bottles.

Gibbs [4] has shown that a zymogen is present in solution in the

[4] *This Journal, Sec. A* (1911), **6**, 99–206.

sap and that atmospheric influence causes the separation of white, flocculent invertase which rapidly attacks the sucrose present. He recommends lining the interior of clean tuquils with thick lime cream, and states that sap collected in receptacles so treated will remain unchanged for a longer period than ten days. We have found that sap collected early in the season of flow may be preserved in a satisfactory manner by this means, provided the interval between placing the tuquil in position on the palm and removing the accumulated juice be not over twelve hours. There is no doubt but that invertase action is effectively stopped in alkaline solution. The principal objection to this method of collection lies in the fact that large amounts of lime are absolutely essential and that an even distribution of alkalinity is uncertain. The latter difficulty is inherent in this method of collection and preservation. The tendency of juice dropping slowly into tuquils containing lime is to stratify. The first juice dissolves relatively large amounts of lime, and consequently attains a density considerably higher than the fresh inflowing sap. These heavy layers remain at the bottom, and are gradually covered with juice containing less and less lime until a point of neutrality is reached. This tendency is counteracted to a greater or less extent by the lime clinging to the sides of the tuquil, but, if this has been carelessly applied or if the cream used was of insufficient consistency, the desired result is seldom accomplished. The upper portion of neutral juice is rapidly acted upon by the invertase present, and subsequently undergoes fermentation, the harmful results of which need not be mentioned in detail. Not only is sucrose destroyed, but invert sugar is formed, and the soluble lime salts resulting from acid fermentation render the juice difficult to handle in boiling and greatly reduce the percentage of available granulated sugar.

A large number of trials served to show that many of the lime-coated tuquils contained acid-top layers of juice after twelve-hour collections, and that this was the case in practically all tuquils after twenty-four hours on the palm. The latter were always covered with froth, and had developed a disagreeable odor characteristic of fermented tuba. A simple and successful method for obviating this difficulty will be discussed later.

OTHER NIPA ENZYMES

We observed that many samples of nipa juice, although uniformly alkaline with lime, showed a gradual loss of sucrose, while other samples could be so preserved for long periods of time without change. Samples of juice originally containing 15 per

cent sucrose gradually deteriorated until after two weeks they contained only 0.5 per cent. The Brix decreased correspondingly, while the small amounts of invert sugar originally present completely disappeared. A careful bacteriological examination by E. L. Walker of the Bureau of Science showed these samples to be practically sterile. The only plausible explanation of this peculiar behavior seemed to be based upon the presence of enzyme activity. We have found that the nipa palm actually does elaborate a very active enzyme of the peroxidase type. Slices of the plant immediately give a dark blue with tincture of guaiacum and hydrogen peroxide and characteristic colors with all the specific tests for this class of enzymes. The speed with which these colors are developed indicates an activity of unusual magnitude. The peroxidase is distributed throughout the entire palm, being present in slight amount in the midrib of the leaf and very strong in the immature fruit. The juice secreted by long flower stalks producing a free flow of sap gave negative tests for the presence of this enzyme, while tuba, from short stems approaching the end of the sap flow, always gave strongly positive tests. It is evident that the character of the juice changes as the season of flow advances, probably due to the varying requirements of the maturing fruit. A careful series of experiments proved beyond doubt that some enzyme capable of destroying both sucrose and invert sugar is present in the nipa palm. It is active in neutral or alkaline solution, but is killed by inorganic acids or heat. Solutions of pure sucrose, both neutral and alkaline with lime, were treated with thin slices of palm tissue containing the enzyme. These solutions were polarized, and the Brix was determined at regular intervals. The sucrose content and density decreased regularly, both in the neutral and alkaline solutions. Tables IV and V show the rate at which sucrose was destroyed in two representative experiments.

TABLE IV.—*Enzyme destruction of sucrose in neutral solution.*

| Time. | Sucrose. | | Brix. |
	Present.	Destroyed.	
Hrs.	*Per cent.*	*Per cent.*	
0	14.40	0	14.5
12	14.15	1.07	....
24	13.90	3.47	14.4
36	13.70	4.86	....
48	13.40	6.94	14.2
60	13.20	8.33	....
72	13.00	9.72	14.0

TABLE V.—*Enzyme destruction of sucrose in alkaline solution.*

| Time. | Sucrose. | | Alkalinity, gram CaO per 100 cc. | Brix. |
	Present.	Destroyed.		
Hrs.	*Per cent.*	*Per cent.*		
0	11.2	0	0.537	13.9
12	10.9	2.68	----------	----------
24	10.6	5.36	0.434	13.3
36	10.4	7.14	----------	----------
48	10.2	8.93	0.409	13.2
60	10.1	9.82	----------	----------
72	9.9	11.61	0.397	13.1

Both of the above solutions gave strongly positive tests for peroxidase at the end of seventy-two hours. The decreasing alkalinity indicates the formation of acid-decomposition products that combine with the lime and reduce the Brix, partially at least, by actual precipitation of calcium salts. The action of carbon dioxide was excluded in all cases. Solutions, similar in every respect except that they contained no enzyme, underwent no change in composition during this time.

Dextrose and levulose in neutral solution are destroyed by this enzyme at approximately the same rate as in the case of sucrose. Table VI includes data showing the oxidation in neutral solution of nearly 10 per cent of the original dextrose within seventy-two hours.

TABLE VI.—*Enzyme destruction of dextrose in neutral solution.*

| Time. | Dextrose. | |
	Present.	Destroyed.
Hrs.	*Per cent.*	*Per cent.*
0	11.4	0
12	11.1	2.6
24	11.0	3.5
36	10.9	4.5
48	10.8	5.3
60	10.6	7.0
72	10.3	9.7

The destruction of invert sugar proceeds rapidly in solutions containing lime with the formation of many decomposition products and a reduction in alkalinity and Brix. The additional effect caused by enzyme action is relatively small in these cases.

TABLE VII.—*Destruction of dextrose in lime solution without enzyme.*

| Time. | Dextrose. | | Alka-linity, gram CaO per 100 cc. | Brix. |
	Present.	De-stroyed.		
Hrs.	*Per cent.*	*Per cent.*		
0	8.0	0.0	0.280	9.7
12	5.0	38.0		
24	3.2	60.0	0.215	9.3
36	2.1	73.0		
48	1.6	80.0	0.182	9.2
60	1.3	84.0		
72	0.9	88.9	0.145	9.1

TABLE VIII.—*Destruction of levulose in lime solution without enzyme.*

| Time. | Levulose. | | Alka-linity, gram CaO per 100 cc. | Brix. |
	Present.	De-stroyed.		
Hrs.	*Per cent.*	*Per cent.*		
0	6.7	0	0.302	10.0
12	5.3	20.1		
24	4.3	35.8	0.201	9.9
36	3.8	50.0		
48	2.8	58.2	0.151	9.7
60	2.4	64.0		
72	2.0	70.1	0.106	9.5

Tables IV and V serve to bring out clearly the remarkable activity of the enzyme present in nipa, and explain why certain samples of juice, uniformly alkaline with lime, gradually decreased in sugar content. Experiments also showed that nipa sap containing palm tissue suffered an even more rapid loss of sucrose by enzyme action than did the sugar solutions prepared in the laboratory. This was to be expected, as the juice contains a variety of constituents that might well activate the enzyme.

The presence of this active enzyme in the nipa palm has a very important bearing on the commercial production of sugar. A loss of from 5 to 10 per cent of the total sugar due to this cause might be a deciding factor between success and failure, and such a contingency must be guarded against in any commercial undertaking. It would be less important if all juice could be collected from long stalks, flowing freely, and secreting a sap comparatively free from enzyme. However, this is impossible under the conditions that prevail in practice. The contents of many

tuquils must be combined for transportation to the mill, and a few rich in enzyme might thus contaminate a large collection.

Laboratory experiments with tissues of nipa palm showed that the presence of a small amount of sulphite was sufficient effectively to destroy the enzyme. The results of these experiments led us to believe that the addition of sulphite, in small amount, to the lime cream before placing it in the tuquils would result in better preservation of the tuba. The actual results obtained by this means exceeded our expectations, and appear to solve the question of preserving nipa juice. A long series of further studies in the swamps demonstrated that sap collected from very short stems producing only a few hundred cubic centimeters of juice in twenty-four hours could be collected and preserved for over ten days when sulphite had been added to the lime cream in the tuquil. Sap flowing from palms of this type always gave a strong positive test for peroxidase.

EXPERIMENTS IN BULACAN PROVINCE

A number of samples were collected on January 25, 1913, in Hagonoy, Bulacan Province, at the extreme end of the season when the flower stalks were short and had nearly ceased flowing. Small samples were first collected in clean glass bottles and analyzed to show the composition of the fresh sap and its rate of flow. Tuquils were then cleaned, lined with lime cream, and placed on the palms. The collections were made twenty-four hours later and analyzed at once. All these tuquils showed acid layers of juice at the top and much frothing due to fermentation. Tuquils were then lined with lime cream containing a small amount of sodium bisulphite and placed on the same palms. These samples were also collected after twenty-four hours and analyzed. A much smaller percentage showed acid tuba and foaming, and the juice was nearly colorless in every case. None of the first series collected with lime alone contained sucrose after further standing for one day, while those in which sulphite had also been used showed no further change. The latter were then combined to form a composite sample, that was transported to Manila and carbonated to faint alkalinity. The precipitate of carbonate was removed, leaving a bright juice of slightly yellow color and high purity. Tables IX, X, and XI show the results of these analyses.

TABLE IX.—*Analyses of fresh juice.*

No.	Length of stalk.	Juice in 5 hours.	Brix.	Direct polarization.	Sucrose.	Purity.
	cm.	*cc.*		*V.°*	*Per cent.*	
1	60	60	12.2	45.0	11.2	91.8
2	80	55	11.3	40.7	10.1	89.3
3	90	100	11.3	38.1	9.5	84.1
4	90	110	13.7	48.8	12.0	87.6
5	80	90	11.8	42.7	10.6	89.8
6	75	45	14.4	51.4	12.6	87.5
7	80	40	15.5	57.4	14.0	90.3
8	75	70	10.6	33.7	8.4	79.2
9	60	60	12.5	42.1	10.4	83.2
10	50	15	(a)			
11	100	60	13.7	46.5	11.3	82.5
12	90	100	11.6	33.6	8.3	71.5
13	95	80	13.4	47.3	11.7	87.3
14	95	25	13.2	44.4	11.0	83.3
15	90	45	12.5	41.0	10.1	80.8
16	110	120	12.5	42.0	10.4	.83.2
17	80	40	12.3	43.0	10.6	86.2
Average					10.7	84.8

ᵃ Fermented.

TABLE X.—*Analyses of 24-hour collections with lime.*

Composition of uncarbonated samples.

No.	Brix.	Polarization.	Sucrose.	Purity.
		V.°	*Per cent.*	
1	10.0	20.6	5.1	51.0
2	9.3	− 5.0	0.0	
3	9.2	18.7	4.7	51.1
4	11.3	13.7	3.4	30.1
5	9.2	15.6	3.9	42.4
6	12.1	24.6	6.1	50.4
7	10.1	9.0	2.3	22.7
8	9.4	− 2.0	0.0	
9	11.8	23.0	5.7	48.3
10	9.3	− 1.0	0.0	
11	12.2	13.5	3.0	27.1
12	9.8	− 1.0	0.0	
13	12.2	16.0	4.0	32.8
14	10.6	16.5	4.1	38.7
15	6.9	− 5.0	0.0	
16	9.8	20.8	5.2	53.0
17	11.0	26.0	6.5	59.0
Average			3.2	29.4

TABLE XI.—*Analyses of 24-hour collections with lime and sulphite.*

Composition of uncarbonated samples.

No.	Brix.	Polariza-tion.	Sucrose.	Purity.
		$V.°$	Per cent.	
1	12.0	40.1	9.9	82.5
2	8.7	27.7	7.0	80.4
3	11.0	34.1	8.5	77.2
4	13.0	45.6	11.3	86.9
5	11.7	34.5	8.6	73.5
6	11.9	38.1	9.5	79.8
7	14.7	50.2	12.3	83.7
8	10.7	31.2	7.8	72.9
9	12.6	39.6	9.8	77.8
10	12.2	30.8	7.6	62.3
11	13.1	40.9	10.1	77.1
12	10.9	30.8	7.7	70.6
13	12.0	40.1	9.9	82.5
14	11.7	36.7	9.1	77.8
15	12.5	39.6	9.8	78.4
16	11.8	38.9	9.6	82.7
17	11.7	39.6	9.8	83.7
Average			9.3	78.8

The composite sample resulting from the juices tabulated in Table XI showed a rise in purity of 4 after carbonation. Increasing the average of Table XI by this amount gives a purity of 82.8, or only 2 lower than the corresponding average of Table IX, for original juice from the same palms. The sugar content and Brix are decidedly lower, due to dilution caused by the lime and sulphite cream. The behavior of sample 10 is especially noteworthy. The juice flowing from this palm gave a strong reaction for peroxidase, and could not be collected in a sterile bottle for analysis without spoiling. With lime and sulphite the sample appeared to have undergone no deterioration, although the purity of the sample was very low. It is probable that the original juice of this palm was of no value, but the results obtained in an extreme case are significant.

EXPERIMENTS IN OTHER SWAMPS

Experiments on a large scale were carried out in one swamp further to test the efficiency of lime cream and sulphite as a preservative. Unfortunately, these tests were made during the month of February when the nipa in this district produces a small second crop of flower stalks. Consequently, few short stems were encountered, and a large excess of thick lime cream without sulphite appeared to be sufficient for preserving the juice. Little or no peroxidase was found in the sap from these plants. The data obtained are found in Table XII.

TABLE XII.—*Analyses of juice collected during February, 1913.*

Set No. and condition of juice.	Palms.	Time of flow.	Volume per tree.	Rate per palm per hour.	Length of stalk.	Brix.	Polarization.	Sugar.	Purity.	Salt (NaCl).	Alkalinity, gram CaO per 100 cc.	Soap test, gram CaO per 100 Brix.
		Hrs.	*cc.*	*cc.*	*cm.*			*P. ct.*		*P. ct.*		
Set No. 1.												
Original juice	20	1.85	74	40	104	16.8	56.6	13.8	82.1	0.57		
Bottled juice after 10 days						16.1	55.7	13.5	82.6		0.015	0.025
Tuquil juice after 10 days	20	24	1,002	42		16.4	50.6	12.3	75.2		0.007	0.021
Set No. 2.												
Original juice	20	1.12	50	45	92	16.5	57.6	14.0	85.2	0.60		
Bottled juice after 9 days						16.3	54.6	13.3	82.7		0.008	0.040
Tuquil juice after 9 days	17	15.5	677	44		16.6	53.6	13.1	78.8		0.014	0.015
Set No. 3.												
Original juice	11	1.31	46	35	106	16.5	57.6	14.0	85.2	0.69		
Bottled juice after 9 days						16.0	55.0	13.4	83.9		0.007	0.027
Tuquil juice after 9 days	8	15.5	511	33		16.5	50.6	12.3	74.4		0.016	0.047
Set No. 4.												
Original juice	20	1.73	70	40	96	15.7	54.6	13.3	84.9	0.058		
Bottled juice after 8 days						15.6	52.2	12.7	81.6		Acid.	0.019
Tuquil juice after 8 days	15	15.2	732	48		15.6	52.8	12.9	82.7		0.015	0.045
Set No. 5.												
Original juice	20	1.40	33	16	78	18.7	65.6	15.8	85.2	0.65		
Bottled juice after 7 days						18.2	63.0	15.2	83.7		Acid.	0.022
Tuquil juice after 7 days	15	17	560	33		18.7	66.2	16.0	85.5		Acid.	0.082
Set No. 6.												
Original juice	20	1.35	48	36	68	17.9	63.4	15.3	85.2	0.59		
Bottled juice after 6 days						18.0	62.0	15.0	83.3		0.009	0.011
Tuquil juice after 6 days	13	16.4	540	33		18.3	64.7	15.6	85.5		Acid.	0.088

Set No. 7.												
Original juice	14	1.33	40	30	52	15.8	51.2	12.5	82.2	0.38		
Bottled juice after 6 days						15.7	53.2	12.9	82.7		Acid.	0.045
Tuquil juice after 6 days	7	21.7	58.6	27		16.6	57.2	13.9	83.8		Acid.	0.036
Set No. 8.												
Original juice	20	1.11	60	54	66	15.6	55.2	12.5	82.2	0.38		
Bottled juice after 5 days						15.1	50.8	12.5	82.6		Acid.	0.046
Tuquil juice after 5 days	18	5.8	28.1	48		16.3	55.0	13.4	82.4		Acid.	0.033
Set No. 9.												
Original juice	20	1.41	59	42	76	15.8	54.0	13.2	83.4	0.42		
Bottled juice after 5 days						15.2	51.8	12.7	83.2		0.019	0.020
Tuquil juice after 5 days	17	6.5	338	52		17.2	58.0	14.1	82.1		0.001	0.011
Set No. 10.												
Original juice	19	0.89	33	36	60	17.4	59.0	14.3	82.3	0.60		
Bottled juice after 5 days						16.4	54.4	13.5	82.5		Acid.	0.033
Tuquil juice after 5 days												
Average of 10 sets.												
Original juice	18.4	1.38	5.2	38	79.8	16.8	58.5	14.0	83.1	0.58		
Bottled juice after from 5 to 10 days						16.3	55.3	13.5	82.7			0.029
Tuquil juice after from 5 to 10 days		14.9	592	40		17.3	55.1	13.4	80.9			0.028

The data in Table XII were obtained from 10 sets of nipa palms representing about 200 plants. The composition of the juice as it issues from the palm is tabulated under "original juice." Samples of this juice after analyses were preserved by the addition of 10 per cent by volume of lime cream containing 0.5 per cent sodium bisulphite and having a density of 36° Brix. These samples were thoroughly mixed to insure uniform distribution of alkalinity, and were preserved in clean bottles. The composition after varying intervals of time is recorded under the heading "bottled juice."

Juice was also collected from the same palms in tuquils coated with lime cream containing sulphite as above. The contents of these tuquils were poured into bottles at the time of collection, and analyzed after varying intervals. The data so obtained are recorded under the heading "tuquil juice." The sap collected in tuquils from the first 3 sets especially showed acidity in the upper layers. A lime cream of 46° Brix was used in the remaining 7 sets, as this consistency adheres better to the sides of the vessels and lessens stratification.

The samples of juice collected in bottles and subsequently treated with lime and sulphite clearly show that once the juice is uniformly mixed with this preservative no further deterioration of importance will take place. The use of sulphite in the lime cream has the further advantage of adding nothing to the cost of manufacture. The sulphite may be added to the lime at the mill by making the lime cream of proper consistency and running into it the requisite amount of sulphur dioxide. This will obviate the necessity of bleaching when the juice is worked up. The amount of sulphur dioxide best suited to the purpose will have to be determined by experiment in actual practice.

THE MODIFIED BAMBOO TUQUIL

We have carried out a series of experiments using a modification of the bamboo tuquil for gathering nipa juice that gives an even distribution of alkalinity throughout the entire collection. The lime and sulphite cream was placed in the bottom of tuquils, no care being necessary to have a layer clinging to the sides. The juice was then allowed to drop into small funnel tubes reaching to the bottom of the tuquils and terminating in bevel ends to allow free exit of the juice. This resulted in carrying the entire collection of sap to the bottom of the tuquils, where it immediately became alkaline, and future change was permanently prevented. There is no possibility when funnels are used for the formation of dense layers of juice containing a large

excess of lime which prevent fresh juice from reaching the preserving cream. A uniform circulation is accomplished in a simple manner, and the beneficial results are evident.

A further confirmatory test of the lime and sulphite preservative using funnels was made by a competent independent investigator on March 10, 1913. The palms for this test were in Bulacan Province, had very short flower stalks, and had practically ceased to flow. The juice gave a strong positive test for peroxidase, and could not be preserved with lime alone. Very few palms were flowing any juice at this time, and the long distances between available trees made it impractical to study more than those recorded in Table XIII. The figures refer to the juice carbonated in Manila two days after collection.

TABLE XIII.—*Analyses of tuba collected in Bulacan.*

No. of sample.	Volume of juice.	Volume of lime cream used.	Polarization.	Brix.	Sucrose.	Purity.
	cc.	*cc.*	*V.°*		*Per cent.*	
1	150	30	54.8	15.5	13.4	86.5
2	185	40	64.0	18.7	15.5	82.9
3	240	40	44.0	13.4	13.4	81.3
4	230	40	48.0	16.3	11.7	70.5
5	250	40	49.0	19.6	11.8	60.3

Samples 4 and 5 contained no sulphite when tested before carbonation. No attempt had been made to clean the tuquils used in collecting this juice, and it is probable that the greater part of the sulphite was destroyed by the accumulation of organic slime. The above results are of great interest as showing what may be accomplished under the most adverse conditions.

Various other experiments show that all tuquils in which funnels had been used with lime and sulphite cream gave juice alkaline throughout, with a purity about 5 units higher than corresponding collections from the same palms following the old method. Moreover, all tuquils in which funnels were not used contained top layers of acid juice with twenty-hour collections.

The use of the funnel method would involve no great difficulty when applied to the collection of nipa juice on a commercial scale, and has much to recommend it. The bowls for the funnels could be turned out of wood at slight expense, and the stems made from branches of spineless bamboo. The amount of lime actually necessary for preserving tuba is very small, probably not exceeding 1 per cent. A large excess is absolutely necessary when the ordinary tuquil is used, although the greater part

must remain undissolved and be wasted. Moreover, the cream must be thick enough to adhere to the sides of the tuquil, and such a cream is difficult to handle in the swamp. Native workmen are prone to be careless, and unless supervised might slight the application of lime or use excessive amounts.

The tubero could measure a thin lime cream by means of a long-handled bamboo cup, and pour it into the tuquils when funnels were employed. No time would be lost in attempting to coat the interior, as the reason for this precaution would no longer exist. The time necessary for adjusting funnels to catch the dripping juice would not be greater than that spent in applying lime for the old method. A marked decrease in operating expense would result, due to the reduction in the amount of lime used, the great saving of carbon dioxide when the juice is carbonated at the mill, and the small consequent burden on the filter presses. This takes no account of the certainty of obtaining high purity juice under all conditions and the complete absence in this juice of the very objectionable calcium acetate resulting whenever acid fermentation takes place. The presence of neutral lime salts in solution after carbonation necessitates treatment with soda ash for their removal, and is coincident with decreased purity. The amount of these salts affords a valuable index of the efficiency of preservation. Reference to Table XII shows that a properly preserved juice need not contain more than about 0.03 gram of CaO per 100 Brix, a negligible amount.

TRANSPORTATION OF SAP

The character of nipa swamps is such that all transportation must be carried on by water. The native tuberos use bancas (canoes hewn out of a single large log), and penetrate all parts of the swamps in these light-draught boats. In some places it has been necessary to construct artificial waterways, but a natural network of small tide-water streams greatly reduces this expense. The sap at present collected for the alcohol industry is carried from the palm to the distillery in large earthen jars called *tinajas,* or is occasionally emptied directly into the bancas. Neither method recommends itself when the sap is destined for a sugar mill. The ordinary 5-gallon kerosene tins are much lighter and easier to carry from palm to palm than the tinajas, and will probably be the most satisfactory means for the purpose. One tubero can readily carry 2 of these cans, representing the collection of juice from 30 or more tuquils. The filled cans may then be placed in bancas and carried to the mill.

THE MILL

Nipa juice, properly preserved with lime and sulphite, offers no difficulties in the mill. A tank should be provided at the water's edge into which the tubero may pour his cargo of juice for analysis and credit.

The subsequent treatment need differ in no respect from customary sugar practice. The juice breaks readily when carbonated to the proper alkalinity and heated to 100°. The sediment settles promptly, leaving a bright juice requiring no further treatment. The filter cake from the sediment is firm, and may be reduced by washing and steaming to a total sucrose content not exceeding 0.2 per cent.

COST OF NIPA JUICE

The price paid by the distilleries for collecting nipa juice in the ordinary manner is about 8 centavos (4 cents United States currency) per tinaja containing from 30 to 36 liters according to locality. This represents about one-half the total cost of production. Swamps are also frequently worked on equal shares. The nipa-land owners, therefore, expect a return of about 2.50 pesos per 1,000 liters of sap produced. This forms a profitable basis for the manufacture of alcohol and consequently for sugar.

The extra labor incident to liming the tuquils will increase the cost of collecting juice to a slight extent. Where labor may be obtained for 1 peso (50 cents United States currency) per day, we estimate the cost of collection at 30 centavos per 100 liters.

EXTRACTION OF SUGAR

White sugar can be made from nipa juice at a manufacturing cost far less than that of either cane or beet sugar. During mill experiments with large quantities of low-grade juice, we have extracted sugar until the final molasses had an apparent purity of only 50. Since this extraction is at least 10 per cent greater than the beet-sugar practice, it represents a further source of profit. Table XIV shows the percentage of available granulated sugar on total solids for purities of from 80 to 90. These figures are very conservative, and no doubt could be exceeded in a well-controlled mill.

TABLE XIV.—*Available granulated sugar in nipa juice.*

Purity.	Available sugar.	Purity.	Available sugar.
	Per cent.		*Per cent.*
80	60	86	72
81	62	87	74
82	64	88	76
83	66	89	78
84	68	90	80
85	70		

For example, 1,000 liters of juice with a purity of 83.1, Brix of 16.8, and sucrose content of 14 per cent would amount to 1,069 kilograms of juice with 179.6 kilograms of dry substance. From the above table of extraction, 66 per cent, or 118.5 kilograms, of granulated sugar could be obtained from this juice without making any allowance for loss. This represents an extraction of 11.1 per cent. The filter press and unknown loss should not exceed 0.5 per cent, leaving 10.6 per cent, or 113 kilograms of sugar per 1,000 liters of juice.

SUMMARY

Yield of nipa sap.—Nipa palms produce about 40 liters of sap per tree during an average season. A conservative estimate of producing palms may be placed at 750 per hectare, yielding 30,000 liters of juice. The nipa district in the Provinces of Bulacan and Pampanga alone is estimated to contain 18,000 hectares, and many other large areas in various islands are available for sugar manufacture.

Season of flow.—The average season during which sap is available in sufficient quantities to supply a sugar mill covers approximately six months. The daily collections reach a maximum during the second month, and gradually diminish after the third or fourth month.

Quality of sap.—The average nipa sap as it flows from the palm during the season contains about 15 per cent sucrose, and has an apparent purity of not less than 85. Invert sugar is present only in traces. About 0.5 per cent of sodium chloride slightly reduces the purity without lowering the extraction of sugar, as it is classed among the nonmelassigenic salts. Waxes, acids, pectins, and other foreign material are practically absent. The sap contains active enzymes of the invertase and peroxidase types, the latter being present only during the final period of

secretion. This peroxidase is capable of oxidizing sucrose and invert sugar in either neutral or alkaline solution.

Collection and preservation of sap.—Nipa sap may be collected without appreciable deterioration in bamboo joints or tuquils containing lime cream and sulphite. The latter may be added to the lime at the mill by passing the requisite amount of sulphur dioxide into a lime cream of proper consistency. The presence of this additional preservative in the lime cream will destroy the enzymes present and prevent deterioration of the sap. It also avoids the necessity of further bleaching. The use of small funnels for conveying the inflowing juice to the bottom of the tuquils avoids stratification and results in more perfect preservation. The additional expense attendant upon their use is slight, and more than counterbalanced by the resulting advantages.

Cost of collection.—Nipa sap can be collected and delivered to a mill on a commercial scale with negligible loss of sucrose and decrease in purity for approximately 3 pesos (1.50 dollars United States currency) per 1,000 liters.

Extraction of sugar.—Approximately 115 kilograms of commercial white sugar polarizing at from 99° to 99°.5 can be recovered from 1,000 liters of sap possessing average composition. No important modification of methods now used in sugar practice will be necessary. Furthermore, no expense corresponding to the grinding of cane or the extraction of beets need be included in the cost of manufacture. The lack of fuel caused by absence of bagasse may be largely overcome by utilizing the cheap and plentiful wood of mangrove swamps.

Cost of manufacture.—Manufacturing sugar from nipa sap will be less expensive than from cane or sugar beet. It is believed that data presented in this paper will form a sufficient basis for calculating costs and profits.

Area of swamp necessary for a 10-ton mill.—About 9,000 liters of nipa sap will be required to produce 1 metric ton of 96° sugar; therefore, a 10-ton mill running at full capacity will necessitate 90,000 liters of sap daily. One hectare of nipa swamp yielding 30,000 liters of juice per season should produce from 200 to 250 liters per day during the months of maximum flow. Therefore, about 450 hectares of good producing swamp would supply such[5] a mill operating at full capacity during the height of the season. Many distilleries at the present time are receiving a larger vol-

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[5] The former estimate (Gibbs, *loc. cit.*, 142) was based upon 2,000 plants per hectare; that is, on the assumption that all plants fruit each year, which is not the case.

ume of juice per day than is required in this estimate. Some of the factors concerning the yield of sap per hectare and the cost of production cannot be accurately determined, but we have investigated this phase of the problem as thoroughly as possible, and have allowed ample margins of safety in every case. A mill designed to manufacture sugar from nipa juice will also be available during that portion of the year when no sap is flowing for refining Philippine sugars in which there is a reasonable profit.

Every indication is for the establishment of a successful industry, and the unfavorable criticism of H. C. Prinsen Geerligs[6] seems unwarranted.

The Bureau of Science will gladly furnish samples of nipa sugar to any one interested.

NOTE.—A further study of the various enzymes present in the nipa palm is in progress to determine, if possible, the exact nature and action of the one responsible for the destruction of sugar.

[6] *Rep. Eighth Int. Cong. Applied Chem.* (1912), 27, 60.

THE ABSORPTION SPECTRA OF VARIOUS PHTHALIDES AND RELATED COMPOUNDS

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Fifteen text figures

Phthalic acid is the parent substance from which a large number of condensation products are obtained that have long occupied a prominent position in chemical discussions. The marked change of color exhibited by the phthaleins upon salt formation has given these compounds a prominent position in all theories regarding constitution and color. The rapid progress in spectroscopic investigation and the ever increasing volume of data available concerning the relation between molecular structure and optical activity has resulted in broadening our conceptions of color changes and modifying our ideas of the underlying causes. Before the absorption spectra of complex substances such as the phthaleins can be rationally interpreted, it is essential to have considerable data relative to similarly constituted compounds possessing simple structures not subject to molecular rearrangement in the quinoid-benzenoid sense. Many of the phthalids are suitable for the purpose, and therefore form the basis of this investigation. Since many simple phthalids of definite, fixed structure dissolve in concentrated sulphuric acid with the production of color, this solvent was included for comparison with absolute alcohol.

DESCRIPTION OF THE ABSORPTION SPECTRA

PHTHALIC ACID

$$C_6H_4 \begin{cases} COOH \\ COOH \end{cases}$$
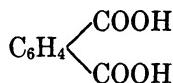
Phthalic acid in ordinary solvents has been studied by many observers and its absorption spectrum been found to show a band heading at $\frac{1}{\lambda} = 3700$. The solution in sulphuric acid exhibits a very different spectrum. Here two well-marked bands make their appearance (fig. 1).

That nearer the red heads at $\frac{1}{\lambda} = 3300$, and the second in the benzene region shows at $\frac{1}{\lambda} = 3800$. Both bands exhibit

more persistence than that given by the alcohol solution, and appear at lower concentration. Both solutions show a purple
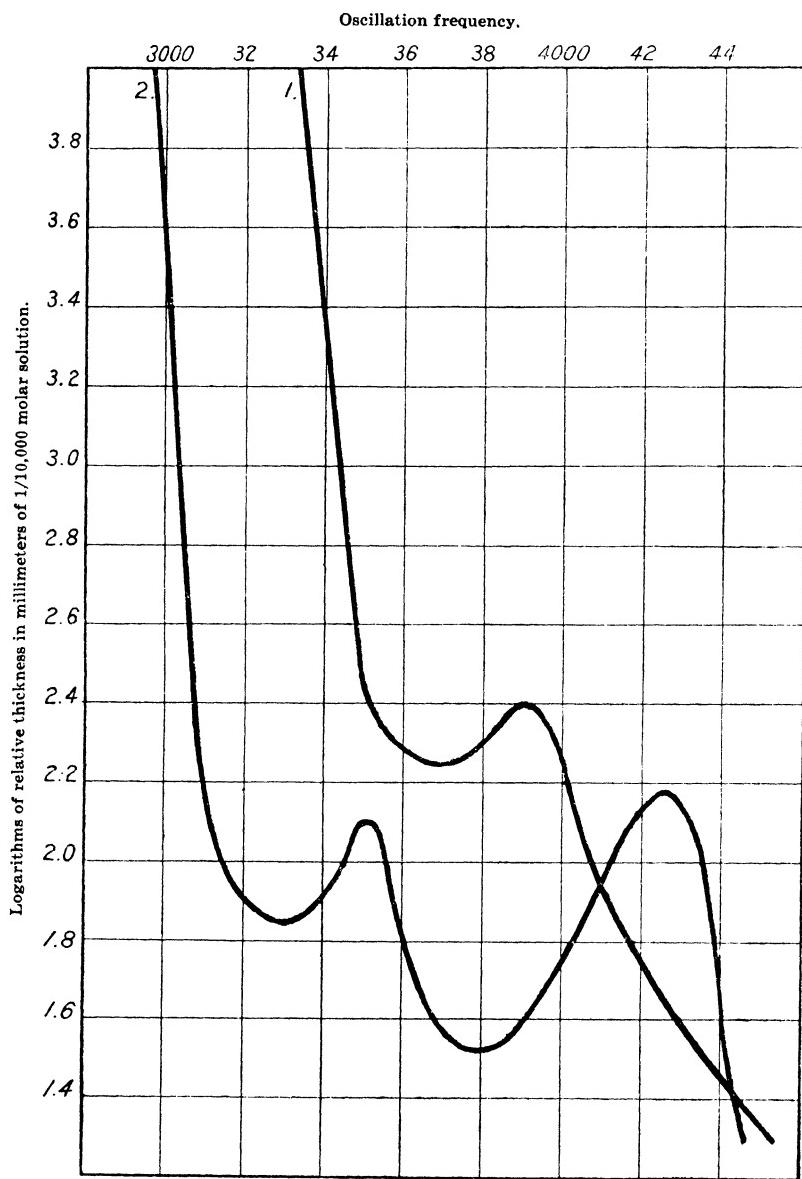
FIG. 1. *Curve 1.* Phthalic acid in alcohol. *Curve 2.* Phthalic acid in sulphuric acid.

fluorescence under the iron-nickel arc, that noticed with alcohol being rather faint compared to the decided color emitted by the sulphuric acid solution.

PHTHALIC ANHYDRIDE

$$C_6H_4 \underset{C=O}{\overset{C=O}{\diagup\diagdown}} O$$
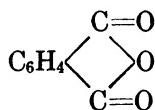
The absorption spectrum of phthalic anhydride was studied in glacial acetic acid solution to avoid any possibility of disrupting the lactone ring. It shows a small band heading at $\frac{1}{\lambda} = 3440$, very similar in outline and persistence to that given by phthalic acid, but less refrangible (fig. 2). This solution is not fluorescent to a noticeable degree.

The anhydride in sulphuric acid fluoresces purple under the arc, and gives an absorption spectrum identical with that of phthalic acid in the same solvent.

MALEIC ANHYDRIDE

$$\begin{array}{c} H\,C-C=O \\ \| \qquad\ \ \diagdown O \\ H\,C-C=O \end{array}$$
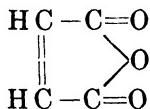
The anhydride was prepared from malic acid according to directions given by van der Riet[1] and recrystallized from ether and from chloroform until pure. The solution in glacial acetic acid shows a band of very slight persistence heading at about $\frac{1}{\lambda} = 3400$ (fig. 3).

The solution in sulphuric acid shows even less selective absorption, with a step-off at about $\frac{1}{\lambda} = 3500$ to 3900.

PHTHALIDE

$$C_6H_4 \underset{C=O}{\overset{C=H_2}{\diagup\diagdown}} O$$
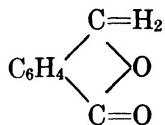
Phthalide was made both by reducing phthalyl chloride[2] and from phthalimide.[3] Both products were purified by repeated boiling with bone black and recrystallization from water. This was necessary to remove traces of resinous impurities that give

[1] *Ann. d. Chem.* (Liebig) (1894), 280, 216.
[2] *Ber. d. deutsch. chem. Ges.* (1877), 10, pt. 2, 1445.
[3] Graebe, *Ann. d. Chem.* (Liebig) (1888), 247, 291.

color with alkali. The absorption spectrum of pure phthalide in alcohol shows a well-marked band heading at $\frac{1}{\lambda} = 3680$. The
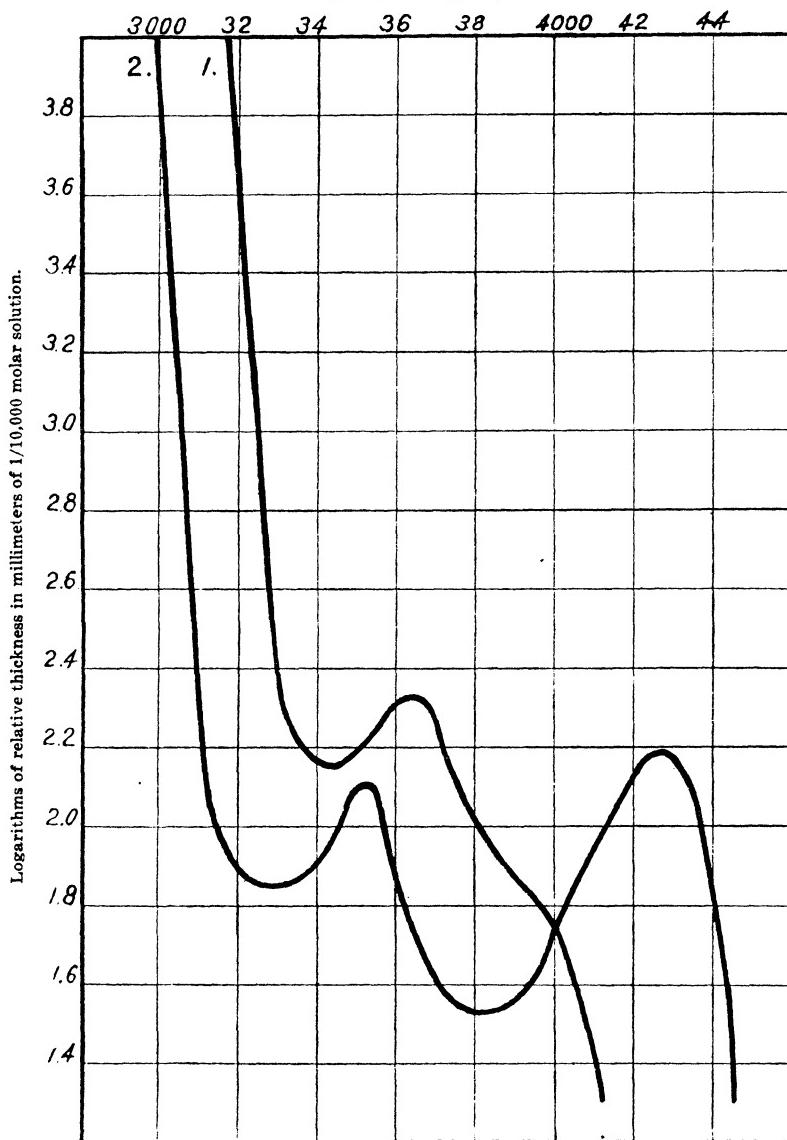
FIG. 2. *Curve 1.* Phthalic anhydride in glacial acetic acid. *Curve 2.* Phthalic anhydride in sulphuric acid.

spectrum is not altered by the addition of one equivalent of sodium ethoxide. The solution in sulphuric acid shows faint

Oscillation frequency.
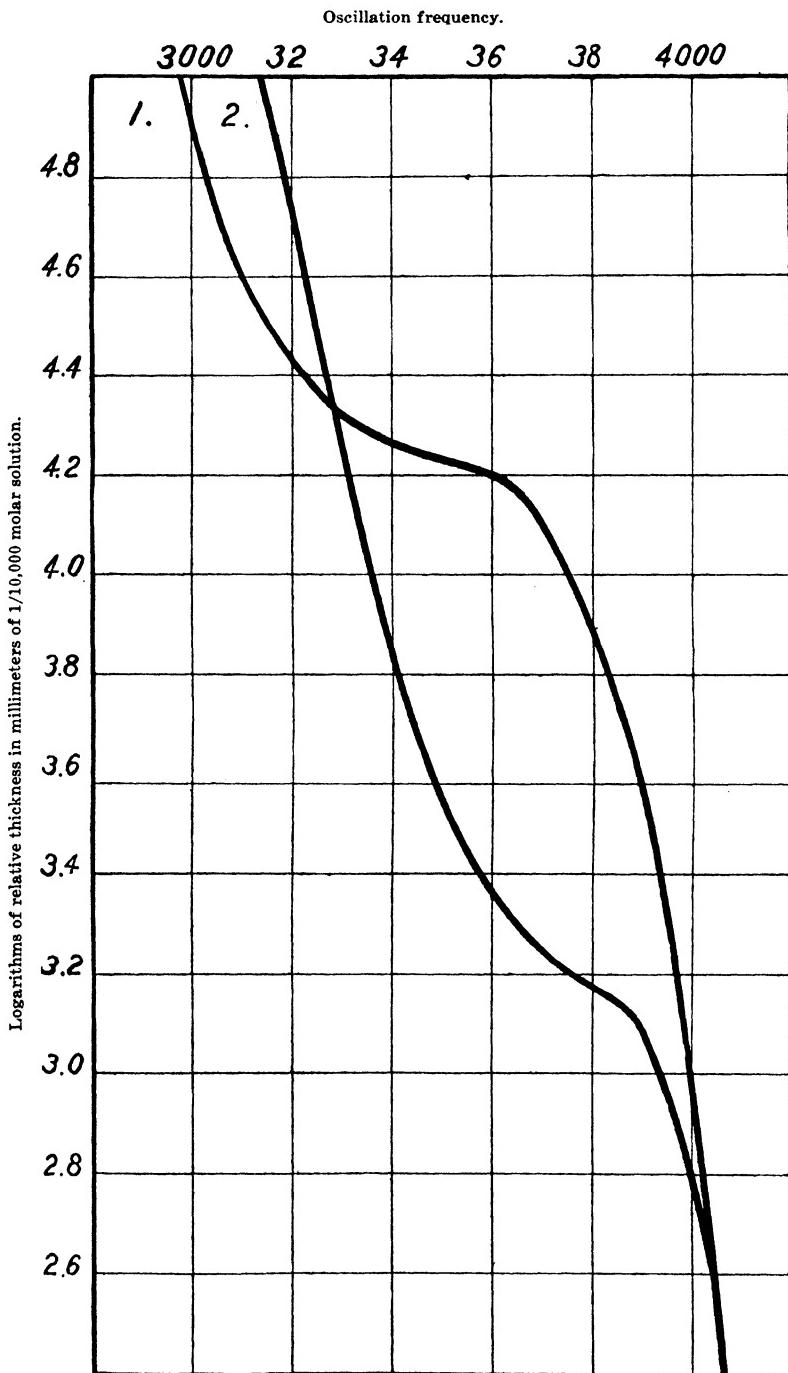
FIG. 3.　*Curve 1.* Maleic anhydride in glacial acetic acid.　*Curve 2.* Maleic anhydride in sulphuric acid.

purple fluorescence, with two bands, one heading at $\frac{1}{\lambda} = 3400$

and a more persistent band at $\frac{1}{\lambda} = 4000$ (fig. 4).

The two preparations of phthalide showed no differences, and were evidently identical.

Oscillation frequency.
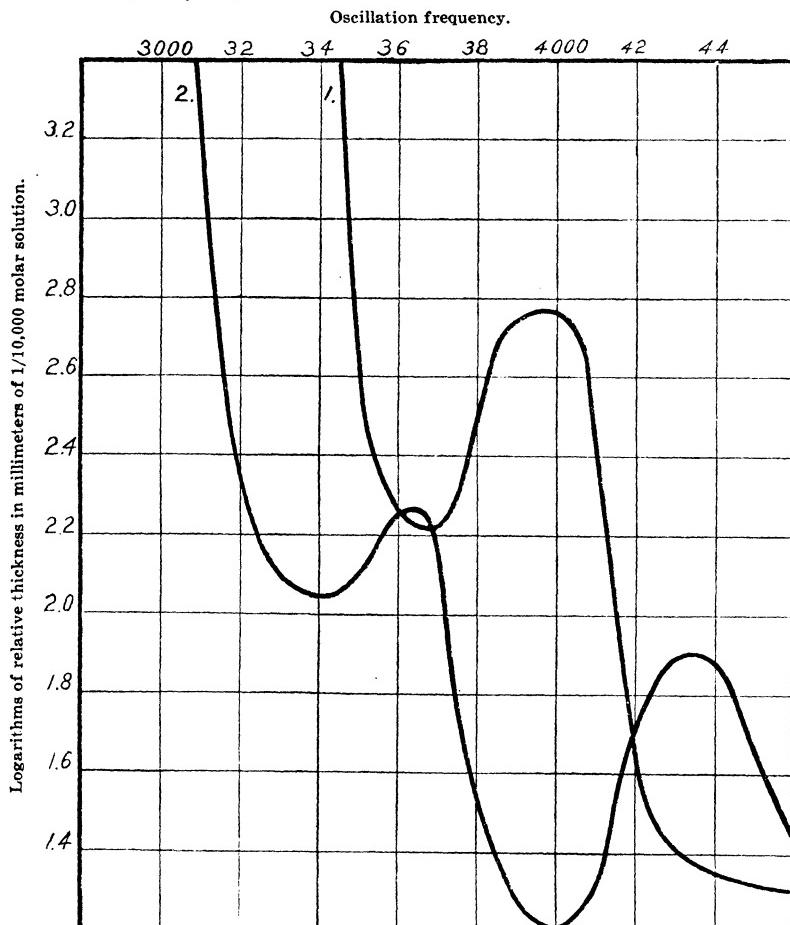
FIG. 4. *Curve 1.* Phthalide in alcohol. *Curve 2.* Phthalide in sulphuric acid.

PHTHALIMIDE

$$C_6H_4 \diagup \begin{matrix} C=O \\ \diagdown NH \\ C=O \end{matrix}$$
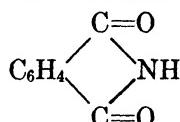
Phthalimide in alcohol shows a well-marked absorption band heading at $\frac{1}{\lambda} = 3460$ and incipient benzene bands (fig. 5).

The addition of alkali causes a broadening of the band and a reduction in persistence, until, in the presence of 5 equivalents

Oscillation frequency.
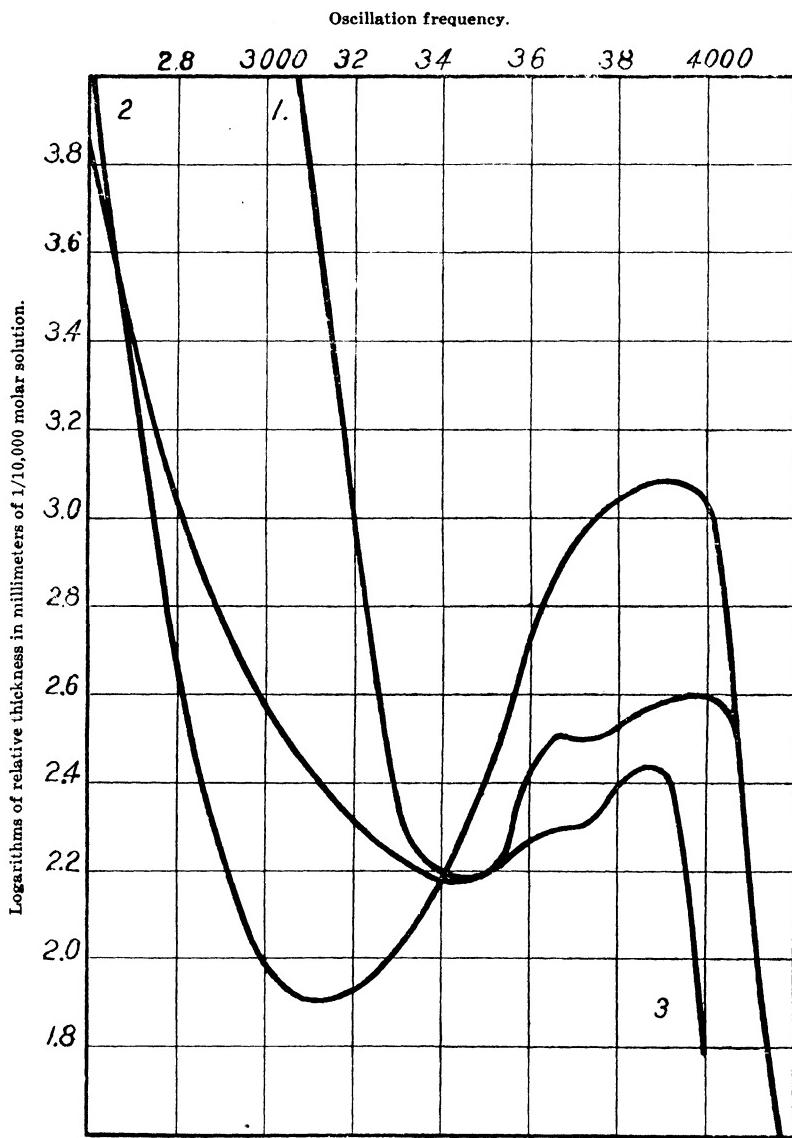
FIG. 5. *Curve 1.* Phthalimide in alcohol. *Curve 2.* Phthalimide in sulphuric acid.
Curve 3. Phthalimide in alcohol + 5 equivalents of sodium ethoxide.

of sodium ethoxide, the general absorption closely approaches the visible region of the spectrum. The band is broad and shallow, but shows no change in the position of its head.

The sulphuric acid solution fluoresces green, and also gives a single band that heads nearer the red at $\frac{1}{\lambda} = 3120$, and shows remarkable persistence:

PHTHALIMIDENE

$$C_6H_4 \left\langle \begin{array}{c} C\!=\!H_2 \\ \\ C\!=\!O \end{array} \right\rangle NH$$
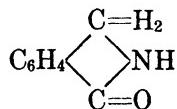
Phthalimidene was prepared from phthalimide[4] and purified similarly to the preceding compound. The alcohol solution gives two absorption bands, a very narrow one heading at $\frac{1}{\lambda} = 3600$ and a broader one slightly more refrangible at $\frac{1}{\lambda} = 3720$. The spectrum is not altered by the addition of one equivalent of sodium ethoxide (fig. 6).

The sulphuric acid solution also gives two bands, a shallow one at $\frac{1}{\lambda} = 3520$ and a well-marked one at $\frac{1}{\lambda} = 4040$.

NITROSOPHTHALIMIDENE

$$C_6H_4 \left\langle \begin{array}{c} C\!=\!H_2 \\ \\ C\!=\!O \end{array} \right\rangle N\!\cdot\!NO$$
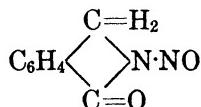
Nitrosophthalimidene, prepared from phthalimide by the action of nitrous acid,[4] was obtained in long yellow needles after recrystallization from dilute alcohol. The absorption spectrum in alcohol is complicated and contains three bands. The color band heading at $\frac{1}{\lambda} = 2320$ is very well marked and of considerable persistence. A shallow band shows at $\frac{1}{\lambda} = 2940$, and the third heads at $\frac{1}{\lambda} = 3820$ (fig. 7).

The addition of one equivalent of sodium ethoxide produces a decided change in color, and shifts the bands to $\frac{1}{\lambda} = 2160, 2940,$ and 3480. The intermediate band now appears at much greater dilution, and is more persistent.

[4] Graebe, *loc. cit.*

Oscillation frequency.
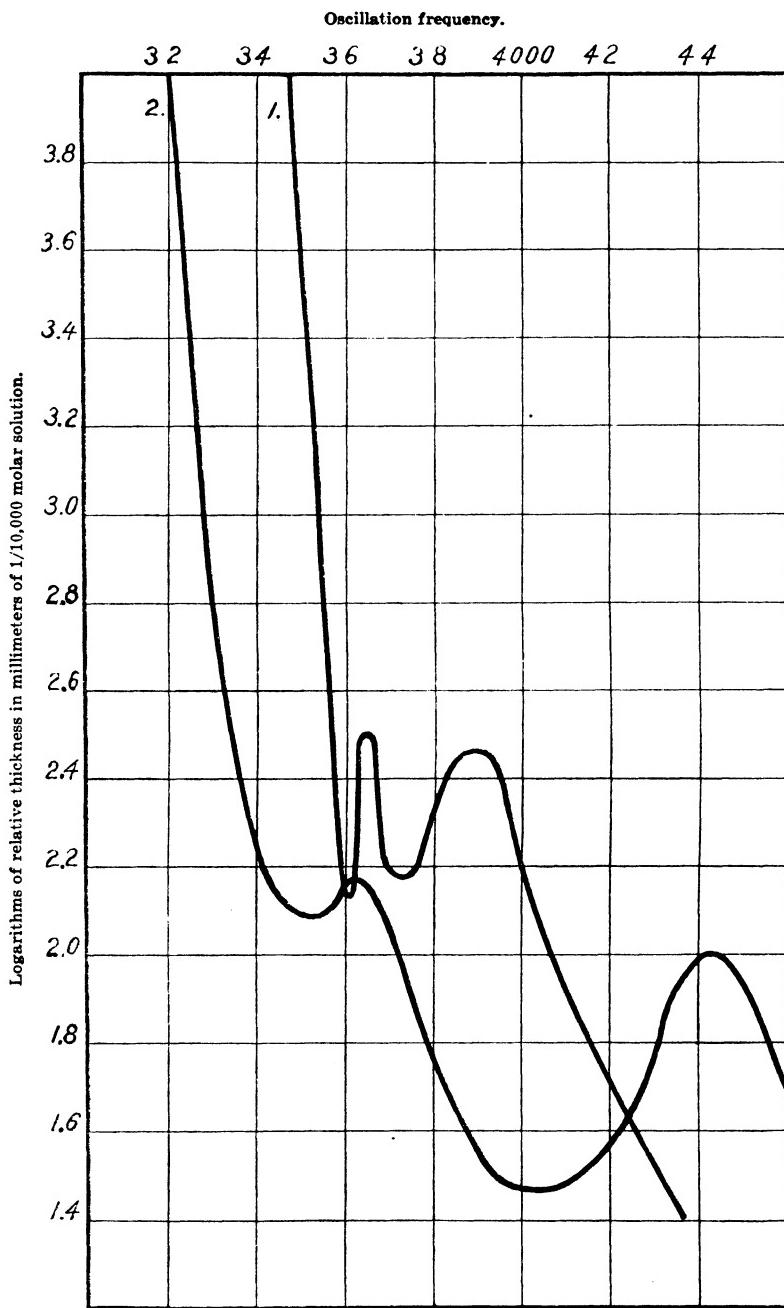
FIG. 6. *Curve 1.* Phthalimidene in alcohol. *Curve 2.* Phthalimidene in sulphuric acid.
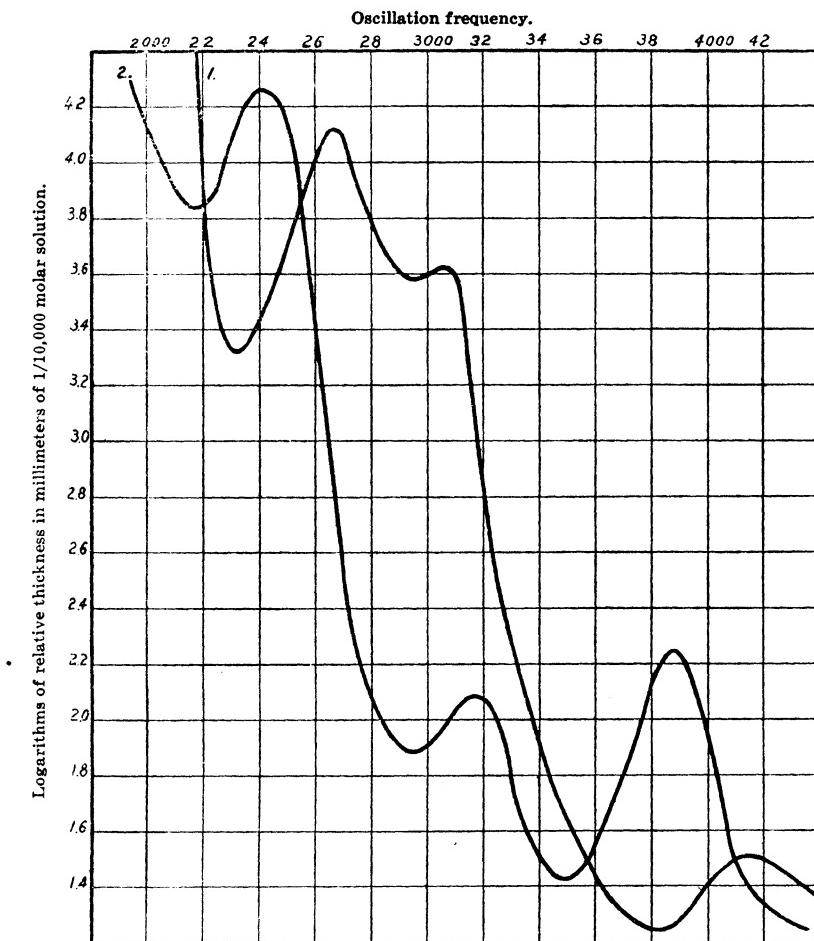
FIG. 7. *Curve 1.* Nitrosophthalimidene in alcohol. *Curve 2.* Nitrosophthalimidene in alcohol + 1 equivalent of sodium ethoxide.

BENZYLIDENE PHTHALIDE

$$C_6H_4 \underset{C=O}{\overset{C=CH \cdot C_6H_5}{\diamondsuit}} O$$
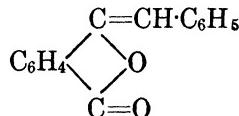
Benzylidene phthalide was prepared from phthalic anhydride and phenylacetic acid[5] and recrystallized from alcohol. The alcohol solution shows a faint blue fluorescence with the arc, and gives two absorption bands heading at $\frac{1}{\lambda} = 2960$ and 3430 that are separated by a very shallow transmitted portion (fig. 8).

[5] *Ber. d. deutsch. chem. Ges.* (1885), **18**, pt. 2, 3470.

The solution in sulphuric acid is yellow, and possesses a beautiful steel blue fluorescence, remarkably vivid under the influence of the arc. Two well-marked bands at $\frac{1}{\lambda} = 2700$ and 3660 were observed in the absorption spectrum.

Oscillation frequency.
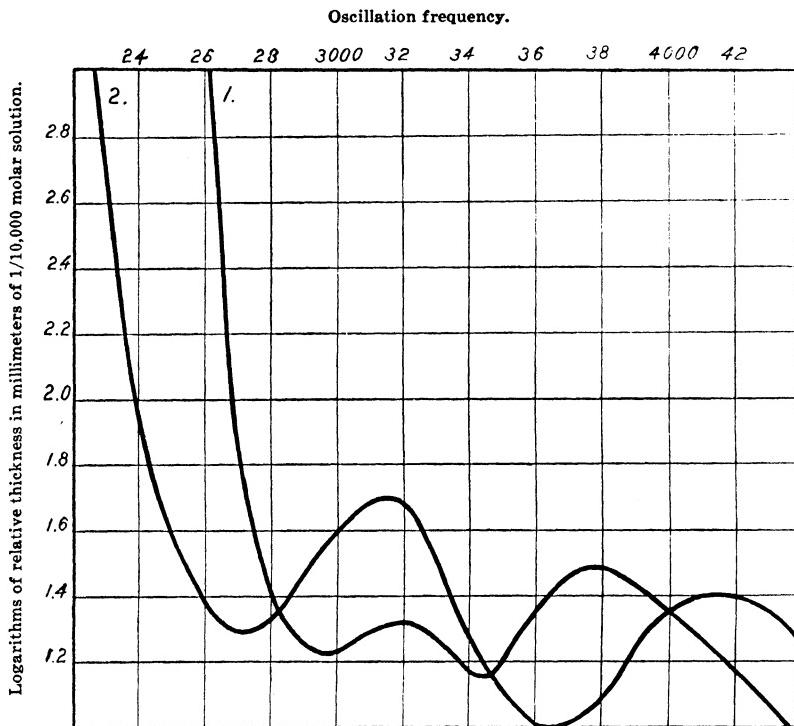
FIG. 8. *Curve 1.* Benzylidene phthalide in alcohol. *Curve 2.* Benzylidene phthalide in sulphuric acid.

CYANBENZYLIDENE PHTHALIDE

$$C_6H_4 \underset{C=O}{\overset{C=C(CN)C_6H_5}{\diamondsuit}} O$$
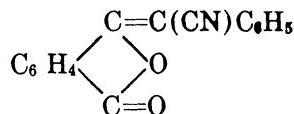
Cyanbenzylidene phthalide, prepared from benzyl cyanide and phthalic anhydride,[6] was recrystallized from alcohol, glacial acetic acid, and methyl alcohol after repeated boiling with bone black. The very faintly colored yellow needles dissolve without apprecia-

[6] *Ibid.* (1885), **18**, pt. 1, 1264.

ble color in alcohol. This solution shows a peculiar absorption spectrum containing a small band heading at $\frac{1}{\lambda} = 2960$ and two step-offs (fig. 9).

The sulphuric acid solution is canary yellow to orange, and shows a greenish fluorescence with the arc. It gives a well-marked band at $\frac{1}{\lambda} = 2800$ and a small band at $\frac{1}{\lambda} = 3820$.
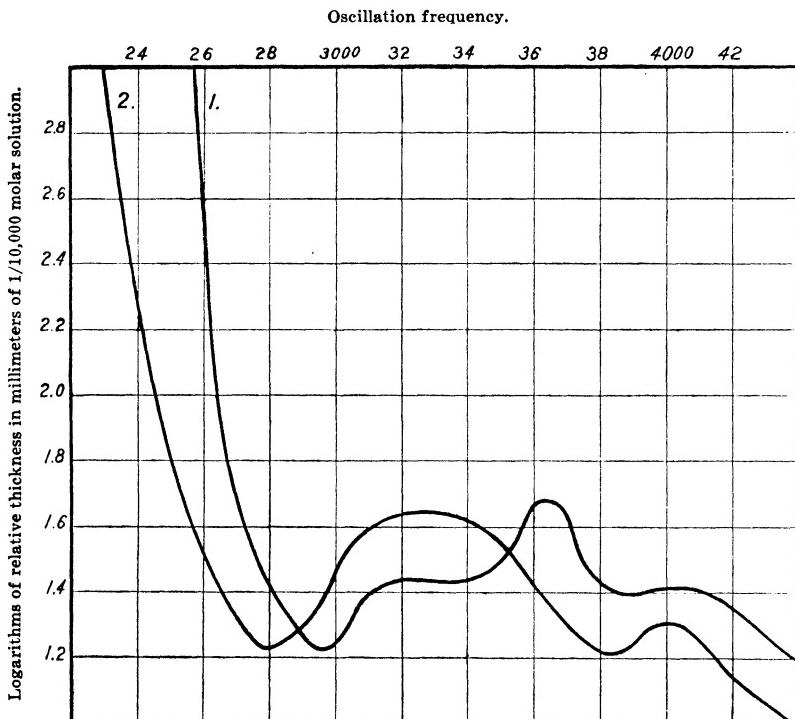
FIG. 9. *Curve 1.* Cyanbenzylidene phthalide in alcohol. *Curve 2.* Cyanbenzylidene phthalide in sulphuric acid.

PHTHALYLACETIC ACID

$$C_6H_4 \diagdown \begin{matrix} C{=}CH{\cdot}COOH \\ O \\ C{=}O \end{matrix}$$
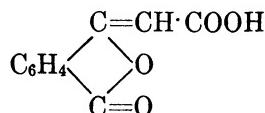
Phthalylacetic acid, made from phthalic anhydride and acetic anhydride,[7] was repeatedly recrystallized from glacial acetic acid

---

[7] *Ibid.* (1893), **26**, pt. 1, 952.

after boiling with bone black until finally obtained as colorless plates. It melted at from 260° to 265° uncorrected, thus corresponding with the determination of Roser.[8] The solution in

Oscillation frequency.
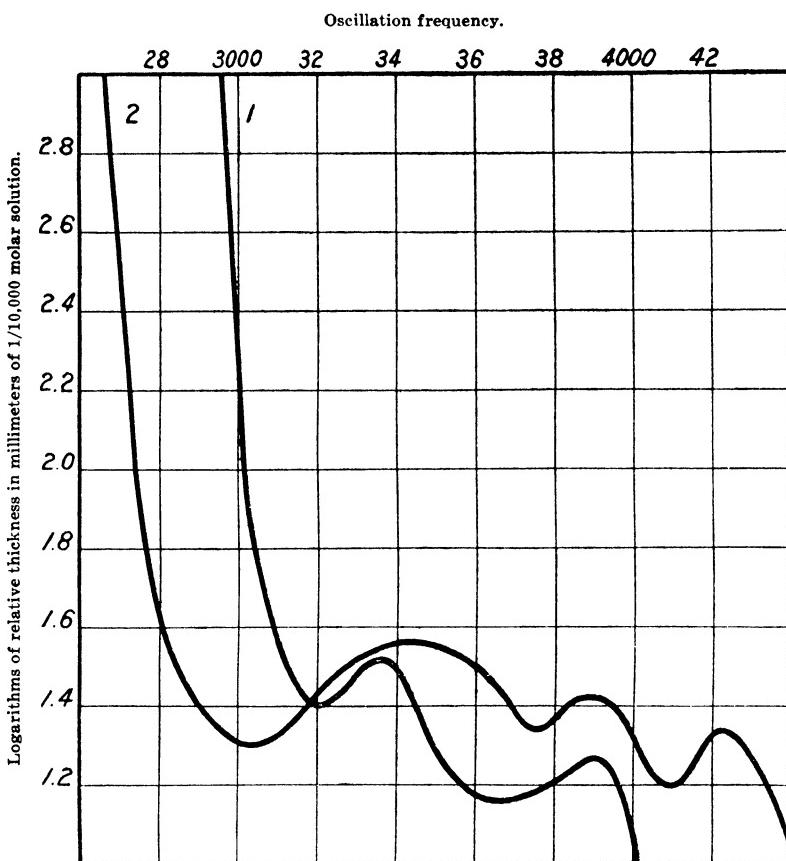
FIG. 10. *Curve 1.* Phthalylacetic acid in glacial acetic acid. *Curve 2.* Phthalylacetic acid in sulphuric acid.

glacial acetic acid is colorless, and shows two bands heading at $\frac{1}{\lambda} = 3200$ and 3660 (fig. 10).

The sulphuric acid solution is light yellow, with faint purple fluorescence under the arc, and is characterized by a well-marked band at $\frac{1}{\lambda} = 3040$ with two small bands at $\frac{1}{\lambda} = 3750$ and 4080.

[8] *Ibid.* (1884), **17**, pt. 2, 2619.

DIPHTHALYL
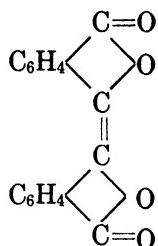
$$C_6H_4 \big\langle \begin{matrix} C=O \\ \\ C \end{matrix} \big\rangle O$$

$$\begin{matrix} \| \\ C \end{matrix}$$

$$C_6H_4 \big\langle \begin{matrix} \\ C=O \end{matrix} \big\rangle O$$

Oscillation frequency.
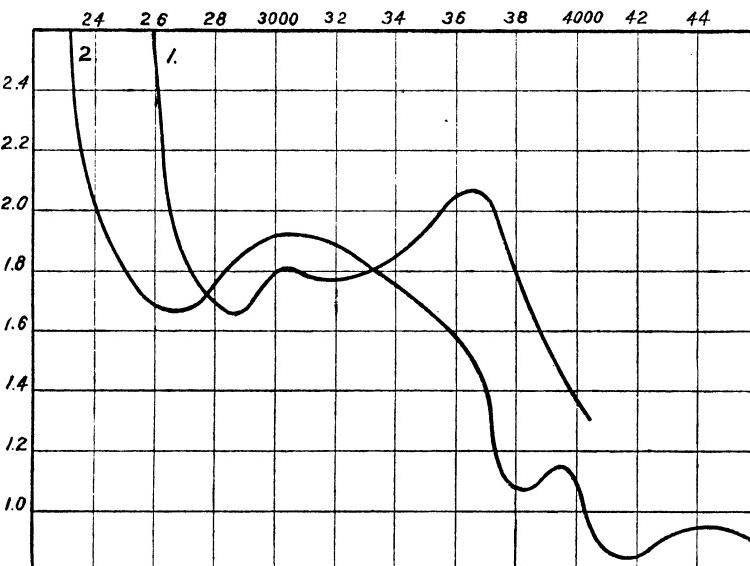
FIG. 11. *Curve 1.* Diphthalyl in glacial acetic acid. *Curve 2.* Diphthalyl in sulphuric acid.

Diphthalyl was made by reducing phthalic anhydride in glacial acetic acid solution with zinc dust.[9] It was recrystallized from glacial acetic acid after boiling with bone black until colorless. The glacial acetic acid solution is colorless, and shows a band at $\frac{1}{\lambda} = 2880$ accompanied by a shallow band at about $\frac{1}{\lambda} = 3200$ (fig. 11).

The sulphuric acid solution is light yellow with bluish

[9] *Ibid.* (1884), 17, pt. 2, 2178.

green fluorescence under the arc, and shows a strong band at $\frac{1}{\lambda} = 2700$. Two smaller bands show in the benzene region at $\frac{1}{\lambda} = 3840$ and 4170.

PHTHALANIL

$$C_6H_4 \underset{C=O}{\overset{C=O}{\diagup\diagdown}} N \cdot C_6H_5$$
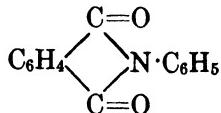
Oscillation frequency.
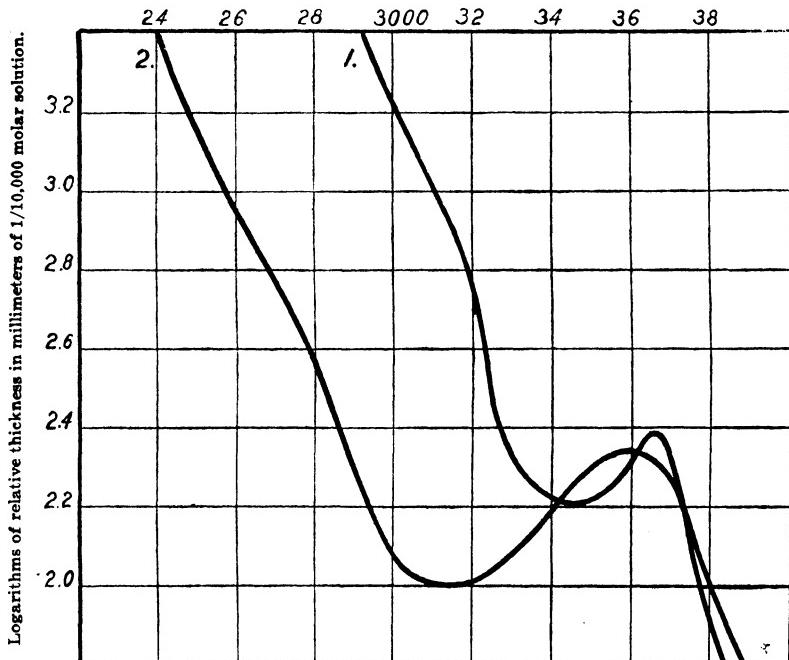
FIG. 12. *Curve 1*. Phthalanil in alcohol. *Curve 2*. Phthalanil in sulphuric acid.

Phthalanil was prepared from aniline and phthalic anhydride by distillation[10] and recrystallized from alcohol and from glacial acetic acid until pure. The colorless alcohol solution gives a single band at $\frac{1}{\lambda} = 3440$ (fig. 12).

The canary yellow sulphuric acid solution also causes a single band that is nearer the red at $\frac{1}{\lambda} = 3120$.

[10] Laurent und Gerhardt, *Jahresber. d. Chem.* (1847–48), 605.

PHTHALOPHENONE

$$C_6H_4\diamondsuit\begin{matrix}C=(C_6H_5)_2\\ O\\ C=O\end{matrix}$$
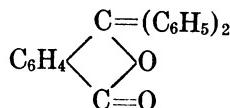
Phthalophenone, from phthalyl chloride and benzene, was purified by repeated crystallization from alcohol. The colorless alcohol solution shows a well-marked band at $\frac{1}{\lambda}=3600$ (fig. 13). The solution in sulphuric acid is orange with a very strong

Oscillation frequency.
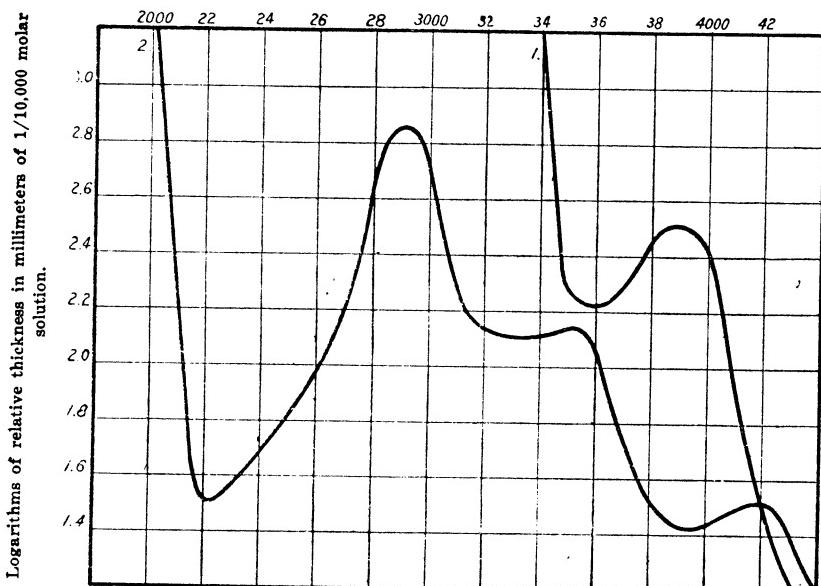
FIG. 13. *Curve 1.* Phthalophenone in alcohol. *Curve 2.* Phthalophenone in sulphuric acid.

color band heading at $\frac{1}{\lambda}=2220$, a shallow band at about $\frac{1}{\lambda}=3320$, and a third in the benzene region at $\frac{1}{\lambda}=3920$.

PHTHALOPHENONE ANILIDE

$$C_6H_4\diamondsuit\begin{matrix}C=(C_6H_5)_2\\ N\cdot C_6H_5\\ C=O\end{matrix}$$
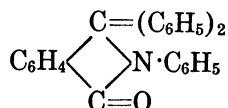
Phthalophenone anilide was prepared from phthalophenone

and aniline.[11] It was recrystallized from alcohol and glacial acetic acid until colorless, and melted at 188° uncorrected. The colorless alcohol solution shows a small band at $\frac{1}{\lambda}$ =3800 (fig. 14).
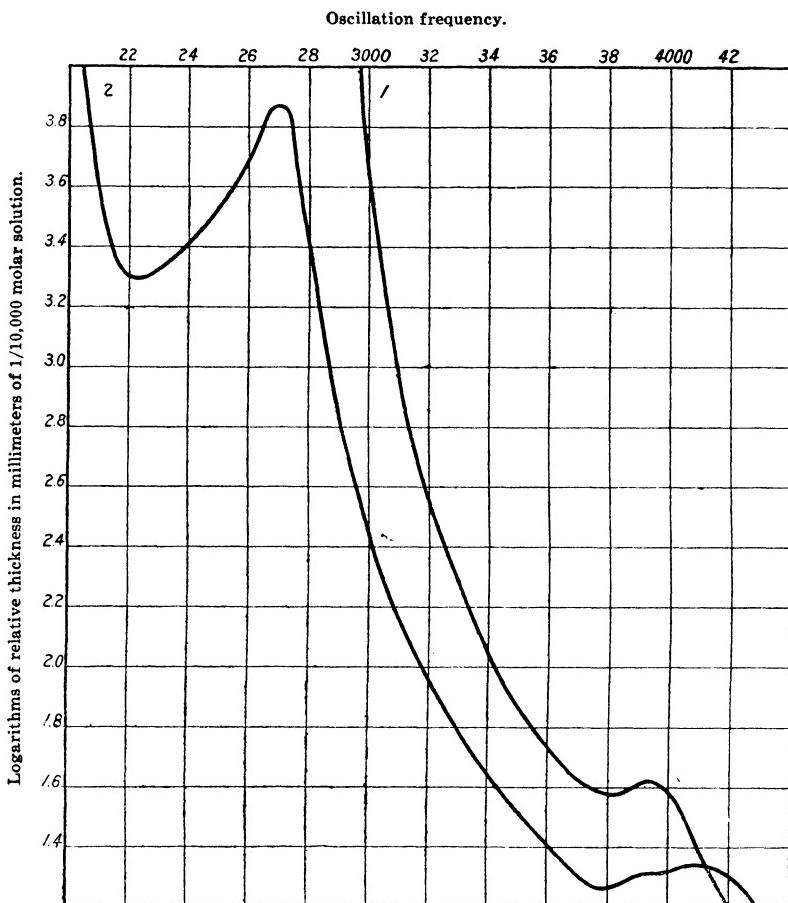
FIG. 14. *Curve 1.* Phthalophenone anilide in alcohol. *Curve 2.* Phthalophenone anilide in sulphuric acid.

The sulphuric acid solution is yellow, with faint greenish blue fluorescence under the arc. A strong color band at $\frac{1}{\lambda}$ =2220 and a small band at $\frac{1}{\lambda}$ =3800 characterize the spectrum.

[11] Fischer und Hepp, *Ber. d. deutsch. chem. Ges.* (1894), **27**, pt. 3, 2793.

PHTHALOXIME

$$C_6H_4 \diamondsuit \begin{matrix} C=O \\ O \\ C=NOH \end{matrix}$$
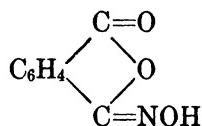
Yellow phthaloxime [12] was prepared from phthalic anhydride and hydroxylamine. It has been shown to give an absorption
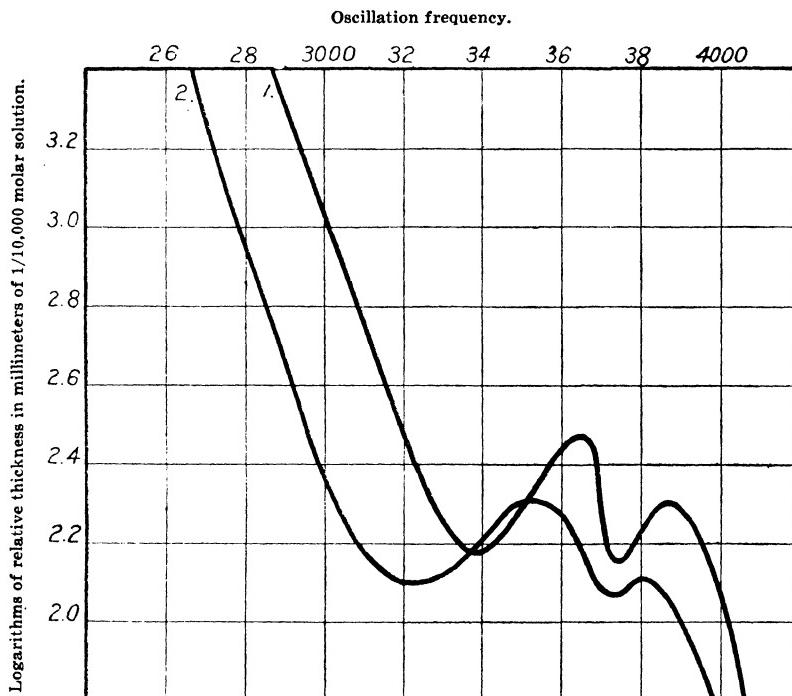
FIG. 15. *Curve 1.* Yellow phthaloxime in alcohol. *Curve 2.* Yellow phthaloxime in sulphuric acid.

spectrum in alcohol solution containing a band at $\frac{1}{\lambda}=3400$ and a small band at $\frac{1}{\lambda}=3740$.[13]

The sulphuric acid solution is faintly yellow, and shows a well-marked band at $\frac{1}{\lambda}=3200$ and a small band at $\frac{1}{\lambda}=3740$ (fig. 15).

[12] Orndorff and Pratt, *Am. Chem. Journ.* (1912), **47**, 89.
[13] Pratt and Gibbs, *This Journal, Sec. A* (1913), **8**, 165.

DISCUSSION OF RESULTS

The substitution of two saturated groups in the ortho position has been shown [14] to modify the absorption spectrum of benzene by causing several of the narrow bands to coalesce into a well-marked band of considerable persistence. When one or both of the substituting groups contain unsaturated centers possessing residual affinity, the position of the resulting band is modified.

Thus ortho xylene shows a broad band heading at $\frac{1}{\lambda} = 3700$, while ortho chloraniline gives a similar band at $\frac{1}{\lambda} = 3450$.[15]

Phthalic acid must be considered as containing two ortho groups possessing little residual affinity. The position of the absorption band corresponds to that of ortho xylene, but the persistence and type are decidedly different. The band cannot, therefore, be attributed to the disubstituted benzene ring alone, but results from the mutual influence of the two carboxyl groups and the ring. The activity of carboxyl is undoubtedly inherent in the doubly bound oxygen with its latent valencies, but the resulting effect is much less than that produced by a true carbonyl grouping. The hydroxyl exerts a counterinfluence that has been demonstrated in many instances and accounted for in a variety of ways. Smedley[16] and others suggest that the carboxyl group may represent a canceling of residual affinities between $=CO$ and $-OH$, which may be indicated by a structure such as
$$\begin{matrix} -C = O \\ \diagdown \diagup \\ OH \end{matrix}$$
Although this graphic representation serves to account for some of the facts in a more or less satisfactory manner, it has not as yet received sufficient confirmation for general acceptance. The extra double bond between the oxygen atoms introduces a condition not possible in phthalic anhydride, but the absorption spectrum of this compound indicates no such radical difference in structure. Some such internal compensation is probably taking place, but thus far an insufficient variety of groups causing an analogous result has been studied to permit any definite conclusions being drawn. *o*-cyanbenzoic, *o*-chlorbenzoic,[17] and *o*-sulphobenzoic [18] acids give absorption spectra of the same type as phthalic acid.
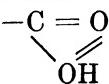
[14] Baly and Ewbank, *Journ. Chem. Soc. London* (1905), **87**, 1355.
[15] Baly and Ewbank, *loc. cit.*
[16] *Journ. Chem. Soc. London* (1909), **95**, 231.
[17] Scheiber, *Ber. d. deutsch. chem. Ges.* (1912), **45**, 2403.
[18] Scheiber und Knothe, *Ibid.* (1912), **45**, 2252.

It was at first thought that an equilibrium might exist between the partial valencies of the two doubly bound carbonyl groups of phthalic acid and that the resulting influence of this conjugation on the benzene ring, although modified and lessened by hydroxyl, might still be of sufficient magnitude to result in a characteristic band. In this event, the elimination of hydroxyl upon anhydride formation should increase the activity of the carbonyl groups and cause phthalic anhydride to produce a band emphasizing this condition. Reference to figs. 1 and 2 shows that the result of removing hydroxyl is to shift the band toward the longer wave lengths without altering the persistence and general type. It is not reasonable to suppose that the equilibrium of the carboxyl groups is the same as that of the lactone ring when these compounds are dissolved in solvents such as alcohol or acetic acid. The fact that the absorption spectra show such great similarity indicates a closer relationship between the benzene ring and the band than between the side chain and the band.

In all of these compounds there exists conjugation between the benzene ring and the substituting groups, and this condition is primarily responsible in every case for the characteristic modification of the benzene spectrum.

This type of conjugation existing between a side chain and a benzene ring was briefly discussed by Thiele [19] in his original paper on partial valency, and his structural formula for phthalic acid appears to be in accord with the absorption spectrum of this compound. However, the peculiar equilibrium of valencies depends upon two doubly bound oxygen atoms in the carboxyl groups, as indicated in the formula:
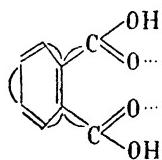
This represents the benzene ring modified by the action of two partial valencies acting with side-chain influences. A similar effect could be ascribed to the lactone ring in phthalic anhydride, and the absorption spectra of these and analogous compounds thus explained. When one double bond is destroyed by substituting two atoms or groups for a carbonyl oxygen, the equilibrium of the resulting molecule could no longer be similarly repre-

[19] *Ann. d. Chem.* (Liebig) (1899), **306**, 130.

sented. Nevertheless, phthalide gives an absorption spectrum closely resembling that of phthalic acid. This serves to emphasize the fact that absorption spectra are caused by types of force equilibria, each giving characteristic manifestations, but which are often incapable of rational expression by the structural formulas employed at present. Phthalids belong to the same type as phthalic acid and its anhydride, and the change from acid to anhydride involves no fundamental alteration in the arrangement of forces within the molecule. This lends support to the equilibrium between phenolphthalein as a lactone and its acid as advanced by Kober and Marshall.[20]

Maleic anhydride possesses a structure corresponding to the side ring of phthalic anhydride during that benzene phase when the double bond occurs between the corresponding carbon atoms.
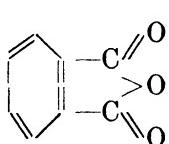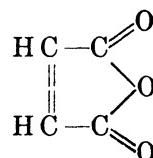
Phthalic anhydride.   Maleic anhydride.

Maleic anhydride, however, shows very little selective absorption, and gives no well-defined band, but rather a rapid extension of transmitted light occurring at high concentration. The effect of introducing this group into the benzene ring corresponds very well with what might be expected. The equilibrium within a compound of two well-defined tendencies, one capable of producing a step-off at about $\frac{1}{\lambda} = 3400$, the other giving well-marked banded absorption between $\frac{1}{\lambda} = 3724$ and $\frac{1}{\lambda} = 4200$, might well result in selective absorption as shown by phthalic anhydride. The character of the resulting absorption would represent an equilibrium between the ortho disubstituted benzenes with saturated groups as in *o*-xylene and the anhydride influence shown in maleic anhydride.

The band is shifted toward the red by the latter influence, and phthalic anhydride, therefore, gives a less refrangible band than *o*-xylene. The effect is less marked in phthalic acid because the influence of the side chain is reduced by hydroxyl groups that cancel a large part of its residual affinity and leave the band nearer the normal benzene region. The opposite effect

[20] *Rep. Eighth Int. Cong. Applied Chem.* (1912), **6**, 157.

is to be noted when the activity of the lactone ring is increased by the introduction of unsaturated centers. Reference to the curves obtained with substituted phthalids of this class clearly shows that in every case an absorption band was found less refrangible than that given by phthalic acid.

One of the carbonyl groups of phthalic anhydride may be replaced by two atoms of hydrogen giving phthalide. This removes one of the double bonds, and would entirely destroy the absorption band if it were due solely to conjugation between the two carbonyl groups. This is not the case, as phthalide shows well-marked selective absorption (fig. 4), and, moreover, the band retains its characteristic type. It heads between that of phthalic acid and its anhydride, thus showing greater activity than the former and less than the latter. The effect of destroying one of the double bonds joined to the lactone ring does not appear ever to result in eliminating the absorption band, but merely modifies its position or persistence. If conjugation between latent valencies is taking place, it must be between the anhydride oxygen and the remaining carbonyl group. This is rendered improbable by the great similarity between the spectra of phthalic acid and its anhydride. Moreover, other acids constituted similarly to phthalic acid, such as phthalylhydroxamic and anilidophthalamic acids in which no anhydride oxygen is present, have been shown to cause a similar absorption band.[21]

The manner in which these latent valencies of a carbonyl group are called into play by near-by atoms or radicals determines the position of the resulting band, its persistence, and the concentration at which it appears. In the case of phthalic anhydride the two carbonyl groups are in the β position, and conjugation of the α diketone type represented by:

$$
\begin{array}{ccc}
\cdot C{=}O: & & \cdot C{=}O \\
\mid & \text{or} & \vdots \quad \vdots \\
\cdot C{=}O: & & \cdot C{=}O
\end{array}
$$
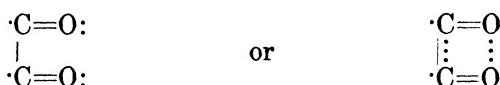
does not appear to be the deciding factor. A very marked difference between the absorption spectra of camphorquinone and methylene camphor [22] shows the effect of disturbing such a condition, although the double bond is not removed. The substitution of methylene with little residual affinity for the active oxygen atom greatly reduces the activity of the entire molecule. The substitution of two hydrogen atoms for the oxygen of

[21] Pratt and Gibbs, *This Journal*, Sec. A (1913), **8**, 165.
[22] Lowry and Southgate, *Journ. Chem. Soc. London* (1910), **97**, 915.

phthalic anhydride giving phthalide effects no analogous change, but merely lessens the activity to a slight degree. The opinion seems justified that some interaction does take place between the two carbonyl groups of the lactone ring, but that it is subordinate to other influences which may be attributed to internal activity of the carbonyl group.

The solutions in concentrated sulphuric acid present very marked contrasts to those where alcohol or glacial acetic acid is employed as solvent. In many cases an entirely new band makes its appearance, and the existing spectrum is further altered by a shift of the original band. Alcohol possesses a low degree of residual affinity, while sulphuric acid shows this property in a marked degree. The effect of the latter solvent is to increase the energy of the solute, thus causing the absorption band to shift toward the longer wave lengths. The only exception noted was with maleic anhydride, in which case the sulphuric acid solution showed less-marked selective absorption than the acetic acid. Here the increased activity was manifested by the band appearing at much lower concentration than in glacial acetic acid solution.

The spectra of phthalic acid and anhydride in sulphuric acid are especially interesting. Both substances give the same curve with two well-marked bands. It was thought possible that the small amount of acid used might be dehydrated and consequently be entirely converted into phthalic anhydride. This is not the case, as was clearly shown by adding a hundredth molar sulphuric acid solution drop by drop to ice-cold absolute alcohol, thus giving a thousandth molar concentration. This solution was photographed at once, and the resulting curve coincided with phthalic acid and not with the anhydride. If the latter compound had resulted from dehydration by the concentrated sulphuric acid, it would not have been hydrolyzed by cold alcohol and its presence could have been detected on the photographic plate. The cancelling effect of hydroxyl in phthalic acid has been prevented by the high residual affinity of the solvent.

It is also significant that in sulphuric acid solutions a band frequently makes its appearance in the benzene region. In the case of phthalic anhydride the original band is shifted from $\frac{1}{\lambda} = 3440$ to 3300 and a benzene band at $\frac{1}{\lambda} = 3800$ is produced. The two opposing influences previously merged and resulting in a single band representative of the equilibrium thus produced have now been resolved by increasing the energy of the lactone

ring until the period between them has reached a point where separation takes place. The band due to a disubstituted benzene ring appears in its characteristic position, while the original absorption shifts in the opposite direction toward the red. The results of this new condition within the molecule are frequently evident to the eye either by the production of color or through fluorescence.

A similar effect may be produced by increasing the residual affinity of the side chain through the actual substitution of active groups. Thus benzylidene phthalide (fig. 8), cyanbenzylidene phthalide (fig. 9), phthalylacetic acid (fig. 10), and diphthalyl (fig. 11) all contain such unsaturated centers, and give absorption spectra characterized by two bands even in alcohol solution. The action of sulphuric acid on these compounds is less marked, but entirely analogous. The less refrangible band is shifted toward the red, while the second approaches the shorter wave lengths characteristic of disubstituted benzene absorption.

Phthalophenone in alcohol shows a single band (fig. 13) similar to the simple phthalide from which it is derived. The effect of replacing two hydrogen atoms by two phenyl groups does not greatly alter the equilibrium. A slight shift of the band toward the red and a decrease in its persistence mark the change. The solution in sulphuric acid, however, is decidedly altered. As before, the single original band is divided, the result being a less refrangible band accompanied by disubstituted benzene absorption. A very strong band of great width and persistence also appears at $\frac{1}{\lambda} = 2220$ in the color region. Oxydiphenyl phthalide and phenolphthalein have been shown to give a similar band in this solvent,[23] but the authors do not comment on the spectra.

The change from a colorless solution to a colored one, or an alteration in the existing color in compounds of the type studied in this paper, cannot be explained logically by the quinoid theory. In many cases such a change in structure is impossible. It is not probable that phthalophenone assumes a true quinoid form when dissolved in concentrated sulphuric acid. A more reasonable explanation may be found in assuming a conjugation between latent valencies of the unsaturated phenyl and carbonyl groups similar to that suggested for the alkali salts of phthaloxime.[24] In this case, the increased energy is supplied by the solvent

[23] Meyer und Fischer, *Ber. d. deutsch. chem. Ges.* (1913), **46**, 80.
[24] Pratt and Gibbs, *This Journal, Sec. A* (1913), **8**, 165.

instead of by introducing a metallic atom into the ring. The resulting equilibrium may be represented by the formula:

$$C_6H_4 \underset{\diagdown C=O}{\overset{\diagup C-Ph^{Ph}}{\diamondsuit}} O \cdots S \overset{\diagup OH}{\underset{\diagdown OH}{\diamondsuit}} \overset{=O}{=O}$$
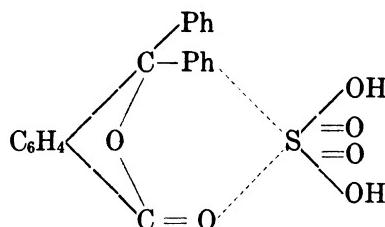
A similar structure may be applied to the phthaleins dissolved in sulphuric acid without invoking quinoid rearrangement. Evidently the condition is unstable, and depends entirely upon the free affinity of the solvent to supply energy for its maintenance. The addition of water destroys this free affinity of the acid, and consequently restores the molecule to its normal colorless configuration.

It is also possible to supply the necessary energy to accomplish this change in equilibrium by introducing more active centers in the molecule as in the case previously considered. Meyer and Fischer [25] have studied the absorption spectra of fluoran and dithiofluoran in alcohol and glacial acetic acid. The former compound gave a curve closely resembling those here shown of the phthalide type as might be expected from its analogous structure, while the latter compound is deep red and gave selective absorption analogous to phthalophenone in sulphuric acid. These authors dismiss the question of the marked difference in color by attributing it to the stronger chromophoric action of the thionyl groups substituted for carbonyl. This increased chromophoric development may be further amplified by considering that the greater free affinity of the sulphur atoms increases the activity of the lactone ring and causes conjugation with the C_6H_4 residue. The result is then very similar to that postulated for phthalophenone in sulphuric acid solution, and may be represented by an analogous structural formula.

I have recently succeeded in preparing a thiophthaloxime that further strengthens this view, as it is a brilliant red and gives deeply colored salts. This interesting compound is now being investigated, and will be described further in a subsequent paper. Other similar colored thio compounds might be mentioned, for example, dithiodiphenyl phthalide.

[25] *Loc. cit.*

Nitrosophthalimidene also typifies a condition of high activity in the side chain, and its absorption spectrum in alcohol contains three bands, one of which is in the color region (fig. 7). The introduction of the unsaturated nitroso group replacing the imido hydrogen has augmented the residual activity of the molecule and has also provided the condition necessary for conjugation. The complete structural formula corresponding to the absorption spectrum may be represented as:

$$C_6H_4\underset{C\diagdown O}{\overset{C\diagup H_2}{\diagup}}N\text{-}NO \rightleftharpoons C_6H_4\underset{C\diagdown O\text{-}\text{-}\text{-}H(M)}{\overset{C\diagup H}{\diagup}}N=NO$$
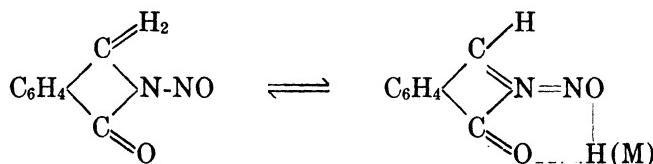
containing a six-membered conjugated ring. The equilibrium is shifted to the right by alkalies with salt formation.

The absorption spectra of the compounds studied in which nitrogen has replaced an atom of oxygen in the side chain are especially interesting, but still more difficult to explain. Phthalimide (fig. 5) and phthalanil (fig. 12) give very similar absorption in ordinary solvents. The bands are shifted toward the longer wave lengths about equal distances in sulphuric acid solution, but the persistence of the band of the former compound is very greatly increased while that of the latter is only slightly greater. The appearance of a benzene absorption band is not evident in either compound in sulphuric acid. Phthalimidine (fig. 6) more closely resembles the phthalic acid type, although even here sulphuric acid does not result in the production of a new absorption band.

Phthalophenone anilide (fig. 14) shows much less pronounced selective absorption than phthalophenone. The sulphuric acid solution of the former still gives a color band heading at the same place as that of the latter, but it appears at very much greater concentration and is only about half as persistent.

The absorption spectrum of phthaloxime is not greatly altered by using sulphuric acid as a solvent, and no new bands are produced.

In every case the introduction of nitrogen in place of oxygen has decreased the effect caused by sulphuric acid. This may be explained readily if the theory regarding the action of sulphuric acid on the phthalids be accepted. The natural affinity between

oxygen and sulphur makes it possible for sulphuric acid to supply considerable energy to the side chain of compounds such as phthalic anhydride and the phthalids. No such affinity exists between the latent valencies of nitrogen and sulphur, as was pointed out by Thiele [26] in explaining the addition of sulphurous acid to quinone diimide where the acid residue attaches itself, not to the nitrogen, but to the carbon. The condition of all these compounds in concentrated sulphuric acid is different from true chemical combination only in degree. The attraction between the acid and the molecule is insufficient to produce a stable addition product capable of isolation, but the first phase of such combination is nevertheless reached. The tendency is most marked in the molecules here considered that still retain either the two original carbonyl groups or equivalent doubly bound atoms possessing attraction for the latent valency of sulphur, and least in those such as phthaloxime where not only has one carbonyl oxygen been removed, but has been replaced by a nitrogen atom. The action of sulphuric acid becomes almost negligible in this case, and the absorption spectra in acid or alcohol are very similar.

Phthalanil retains the carbonyl groups in addition to having nitrogen in the lactone ring, and consequently shows a marked shift in the position of its absorption band by sulphuric acid. No new band is developed in the benzene region, however, as the amount of energy supplied by the acid is not sufficient, in the presence of the opposing nitrogen, to separate the two influences into their components.

When one carbonyl oxygen of phthalanil is replaced by two phenyl groups, the effect is further reduced. The band in the ultra-violet is not shifted by sulphuric acid in this case, and so little energy is supplied to the molecule that only slight conjugation takes place between the remaining carbonyl and the phenyl groups. The color band must head at the same place as it is caused by the same mutual influence, but it now appears at log. 3.3 instead of log. 1.5 and is greatly reduced in persistence.

SUMMARY

1. The absorption spectra of various derivatives of phthalic acid representing the phthalide and lactone type have been studied in ordinary solvents and in concentrated sulphuric acid.

[26] *Ann. d. Chem.* (Liebig) (1899), **306**, 130.

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2. A theory based upon the latent valency of this acid has been advanced to account for the remarkable changes it produces in these spectra.

3. This theory includes the color of phthalids and phthaleins dissolved in sulphuric acid and of the thio derivatives of this type of compounds.

4. The counterinfluence of substituting nitrogen in the side chain is discussed in relation to its effect on absorption spectra.

ILLUSTRATIONS

ANALYSIS AND COMPOSITION OF RED LEAD

By Augustus P. West[1]

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When lead is heated to a temperature of low redness, the monoxide (PbO) is obtained. When the temperature is carefully regulated and kept below the melting point of the monoxide, the product obtained is a yellowish powder known as massicot. If the monoxide is melted during the preparation, the product is a reddish solid known as litharge. The commercial monoxide of lead is a yellow to reddish yellow solid, the color and specific gravity of which vary with the conditions of formation. When lead monoxide is heated in the air at a temperature of from about 300° to 550°, oxygen is gradually absorbed and a red product is obtained known as minium or red lead. At temperatures above 550°, red lead is decomposed to lead monoxide.

Various methods have been proposed for estimating the purity of red lead, but they are all more or less unsatisfactory. Although red lead has been investigated extensively, the exact composition is still an unsettled question. The object of this paper is to describe a method which has been found satisfactory for determining the purity and composition of red lead.

Commercial red lead is usually regarded as a mixture of minium (Pb_3O_4), uncombined lead monoxide (PbO), and small amounts of impurities (such as red clay, barium sulphate, iron oxide, and sand).

Analyses of 16 samples by F. Lux[2] showed the impurities to vary from 1.4 to 13.5 and the uncombined lead monoxide from 2.3 to 42.5 per cent.

D. Woodman[3] in 21 analyses found the uncombined lead monoxide to vary from 8 to 59 per cent.

Woodman's method for determining the purity of red lead consists simply in leaching out the free litharge with lead acetate solution and in determining the red lead by difference.

When minium is treated with dilute nitric acid, it decomposes according to the equation

$$Pb_3O_4 + 4HNO_3 \rightarrow PbO_2 + 2Pb(NO_3)_2 + 2H_2O$$
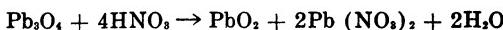
[1] Assistant professor of chemistry, University of the Philippines.
[2] *Zeitschr. f. anal. Chem.* (1880), 19, 155.
[3] *Journ. Am. Chem. Soc.* (1897), 19, 339.

Some of the most accurate methods for estimating the purity of red lead are based on the direct estimation, either volumetrically or gravimetrically, of the lead dioxide thus formed.

The method of Lux, for instance, consists in merely determining the amount of black lead dioxide (PbO_2) and calculating the percentage of minium (Pb_3O_4).

Probably one of the best general methods which has been suggested for determining the purity of red lead is that outlined by Baucher.[4]

This consists in determining insoluble impurities, lead dioxide (PbO_2), and free litharge (PbO), and calculating by difference the combined lead monoxide. In this method the free litharge is determined by leaching with a solution of lead acetate, and consequently the results obtained are not especially accurate.

That these various methods do not give very accurate results is brought out in the following analytical data, in which the percentage of red lead was determined by treating the sample with nitric acid, filtering off the insoluble lead dioxide, drying, weighing, and calculating as minium.

<div align="center">

Sample A.

</div>

	Per cent.	
Insoluble matter	none	
Red lead (Pb_3O_4)	77.44	(equivalent to 27.02 per cent PbO_2)
Free litharge (PbO)	18.54	
Not accounted for	3.99	
	100.00	

77.44 per cent Pb_3O_4 is equivalent to	70.47 per cent Pb
18.54 per cent PbO is equivalent to	17.21 per cent Pb
Total Pb calculated	87.68 per cent
Pb by direct determination	91.37 per cent
Pb not accounted for	3.69 per cent

The figures show a wide discrepancy between the total lead as calculated and the actual lead content. Soluble lead salts were shown to be absent by leaching the sample with hot water and attempting to precipitate the lead as sulphate. Since the above results were obtained in closely agreeing duplicate determinations, it would seem that the error of 3.66 per cent in the calculated total lead content was due to errors in method both in analysis and calculation. Probably the actual percentage of

[4] *Petit Monit. Pharm.*, **47**, 2651.

red lead in the sample is not to be directly computed from the percentage of lead dioxide.

In 1850, Mulder [5] showed that in red lead the percentage of oxygen above that required in lead monoxide varies from 1.16 to 2.67 per cent. Several samples of red lead agreed in composition with the formula Pb_4O_5. In Table I is given the oxygen content of various oxides of lead.

TABLE I.—*Oxygen content of various lead oxides.*

Compound.	Oxygen.	Oxygen greater than oxygen content of PbO.
	Per cent.	*Per cent.*
PbO	7.12	....
Pb4O5	8.81	1.69
Pb3O4	9.35	2.23
Pb2O3	10.39	3.27

According to Mulder's results, it appears that some samples of red lead consist of mixtures of different oxides of lead.

In 1851, Mulder's results were confirmed by Jacquelain,[6] who examined a number of samples of red lead and noticed that the oxygen content varied considerably.

In 1889, Lowe [7] pointed out that both the oxides Pb_3O_4 and Pb_4O_5 may be present in red lead, but that the commercial article containing free extractable PbO probably consists of a mixture of Pb_4O_5 and PbO.

Whether one or both of the oxides Pb_3O_4 and Pb_4O_5 are present in a sample of pure red lead, can be determined in the following manner: By leaching with a solution of lead nitrate, any free PbO can be eliminated, leaving only pure red lead. Now minium when heated above 500° gives lead monoxide and a loss of 2.34 per cent of oxygen. If the compound Pb_4O_5 behave in a similar manner, it would be decomposed according to the equation $Pb_4O_5 \rightarrow 4\,PbO + O$ and the oxygen loss would be 1.76 per cent. Knowing the oxygen loss of a mixture of the oxides Pb_3O_4 and Pb_4O_5, we can calculate the amount of each present in the mixture. However, since the figures representing the loss of oxygen are rather small, the experimental error involved in determining

[5] *Journ. f. prakt. Chem.* (1850), **50**, 438.
[6] *Ibid.* (1851), **53**, 161.
[7] *Dingler's polytech. Journ.* (1889), **271**, 472.

such a factor would make it a somewhat undesirable method. A more practical method will be described later.

Minium is regarded as composed of lead dioxide combined with two molecules of lead monoxide, $PbO_2 . 2PbO$, and a compound of the formula Pb_4O_5 would consist of one molecule of lead dioxide combined with three molecules of lead monoxide, $PbO_2 . 3PbO$; in other words, both compounds may be considered as composed of PbO_2 plus combined PbO.

If red lead consist of a mixture of various oxides such as $PbO_2 . 2PbO$, $PbO_2 . 3PbO$, and free PbO, we can easily determine the various constituents in the mixture as follows:

Decompose the complex oxides with dilute nitric acid. Separate and weigh the resultant black lead dioxide, and calculate the lead monoxide from the lead present in the filtrate. The latter result gives the free plus combined lead monoxide. In a separate sample determine free lead monoxide by leaching with a suitable solvent, and compute the lead monoxide by difference. This method of separation is clearly shown in the following diagram:

Commercial red lead, precipitated by dilute HNO_3.

Total PbO determined as Pb.

PbO dissolved with $Pb(NO_3)_2$ solution.
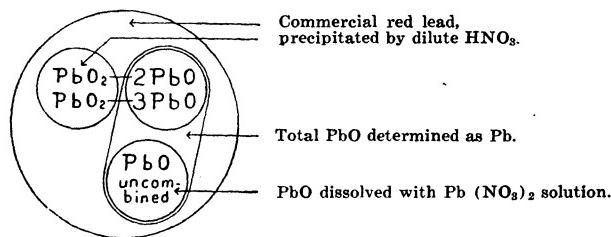
The percentage of lead dioxide plus the percentage of combined monoxide gives the percentage of red lead.

Knowing the percentage of combined lead monoxide, we can calculate the actual amount of each of the oxides Pb_3O_4 and Pb_4O_5 in the following manner:

Suppose an analysis of a mixture of the oxides Pb_3O_4 and Pb_4O_5 shows 70.25 per cent combined PbO. Since

Pb_4O_5 contains 73.68 per cent combined PbO and
Pb_3O_4 contains 65.11 per cent combined PbO,

the percentage of each constituent in the sample may be calculated as follows:

Per cent Pb_3O_4 + per cent Pb_4O_5 = 100
$(0.6511 \times$ per cent $Pb_3O_4) + (0.7368 \times$ per cent $Pb_4O_5) = 70.25$,

which by computation shows 40 per cent Pb_3O_4 and 60 per cent Pb_4O_5, respectively.

Table II shows the combined lead monoxide content corresponding to each of a series of mixtures of the oxides Pb_3O_4 and Pb_4O_5, ranging from pure Pb_3O_4 to pure Pb_4O_5.

TABLE II.—*Mixtures of lead oxides and the corresponding combined PbO content of each mixture.*

Mixture.			Mixture.			Mixture.			Mixture.			Mixture.		
Pb_3O_4	Pb_4O_5	Combined PbO.	Pb_3O_4	Pb_4O_5	Combined PbO.	Pb_3O_4	Pb_4O_5	Combined PbO.	Pb_3O_4	Pb_4O_5	Combined PbO.	Pb_3O_4	Pb_4O_5	Combined PbO.
P. ct.	P. ct.	P. cent.	P. ct.	P. ct.	P. cent.	P. ct.	P. ct.	P. cent.	P. ct.	P. ct.	P. cent.	P. ct.	P. ct.	P. cent.
100	0	65.11	80	20	66.82	60	40	68.54	40	60	70.25	20	80	71.97
99	1	65.19	79	21	66.91	59	41	68.62	39	61	70.34	19	81	72.05
98	2	65.28	78	22	66.99	58	42	68.71	38	62	70.42	18	82	72.14
97	3	65.36	77	23	67.08	57	43	68.79	37	63	70.51	17	83	72.22
96	4	65.45	76	24	67.17	56	44	68.88	36	64	70.59	16	84	72.31
95	5	65.54	75	25	67.25	55	45	68.97	35	65	70.68	15	85	72.39
94	6	65.62	74	26	67.34	54	46	69.05	34	66	70.76	14	86	72.48
93	7	65.71	73	27	67.42	53	47	69.14	33	67	70.85	13	87	72.56
92	8	65.79	72	28	67.51	52	48	69.22	32	68	70.94	12	88	72.65
91	9	65.88	71	29	67.59	51	49	69.31	31	69	71.02	11	89	72.74
90	10	65.97	70	30	67.68	50	50	69.39	30	70	71.11	10	90	72.82
89	11	66.05	69	31	67.77	49	51	69.48	29	71	71.19	9	91	72.91
88	12	66.14	68	32	67.85	48	52	69.57	28	72	71.28	8	92	72.99
87	13	66.22	67	33	67.94	47	53	69.65	27	73	71.37	7	93	73.08
86	14	66.31	66	34	68.02	46	54	69.74	26	74	71.45	6	94	73.16
85	15	66.39	65	35	68.11	45	55	69.82	25	75	71.54	5	95	73.25
84	16	66.48	64	36	68.19	44	56	69.91	24	76	71.62	4	96	73.35
83	17	66.57	63	37	68.28	43	57	69.99	23	77	71.71	3	97	73.42
82	18	66.65	62	38	68.37	42	58	70.08	22	78	71.79	2	98	73.51
81	19	66.74	61	39	68.45	41	59	70.17	21	79	71.88	1	99	73.59
												0	100	73.68

In estimating the purity of samples of red lead, the following method is satisfactory. By determining the amount of combined PbO and referring to Table II, one may ascertain the amount of each of the oxides Pb_3O_4 and Pb_4O_5. The calculated total lead content of the sample checks with the percentage of total lead as obtained by direct determination.

METHOD OF ANALYSIS

a. Insoluble matter.—Baucher's method [8] gives very good results for this determination, and may be carried out satisfactorily in the following manner:

A 2-gram sample is treated with 100 cubic centimeters of 10 per cent nitric acid solution; after a few minutes' boiling, the red lead is completely decomposed, leaving only the black lead

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[8] *Petit Monit. Pharm.*, **47,** 2651.

dioxide. Fifteen cubic centimeters of a cane-sugar solution, prepared by dissolving 1 part of cane sugar in 3 parts of water, are slowly added. On boiling a short time, the lead dioxide is reduced to lead monoxide and dissolves in the nitric acid. The liquid is filtered through a Gooch crucible, and the insoluble residue is weighed. In red lead of good quality there is usually less than 1 per cent of insoluble matter.

b. Free litharge.—The free lead monoxide is best determined by the method of Lowe.[9] This method gives excellent results when carried out in the following manner: A 0.5-gram sample is treated with 100 cubic centimeters of 10 per cent lead nitrate solution. The mixture is digested on a water bath about one hour, after which it is boiled ten minutes, diluted to twice its volume with hot water to dissolve basic salts, and filtered through a Gooch crucible. The residue is then weighed.

c. (PbO₂ + insoluble matter) and (PbO free + PbO combined).—A 0.5-gram sample is treated with 100 cubic centimeters of 10 per cent nitric acid. After heating on a water bath about one-half hour, all the red lead is decomposed to the black lead dioxide; the liquid is then filtered through a Gooch crucible, and the residue of lead dioxide and insoluble matter is weighed. The percentage of insoluble matter having already been ascertained, the difference gives the percentage of lead dioxide.

To the filtrate add 20 cubic centimeters of sulphuric acid (1 part concentrated H_2SO_4 to 5 parts H_2O), evaporate until white fumes are evolved, cool, and add carefully 40 cubic centimeters of water. Now add 100 cubic centimeters of 75 per cent alcohol, stir, and, after the precipitate has settled, filter through a Gooch crucible, dry at 100°, and weigh. If there is considerable insoluble matter present, the precipitated lead sulphate is probably contaminated with foreign matter. In this case more accurate results are obtained by dissolving the lead sulphate in ammonium acetate and reprecipitating.

From the weight of lead sulphate obtained, the percentage of (PbO free + PbO combined) is calculated. Having previously determined the percentage of free lead monoxide, the percentage of combined lead monoxide is obtained by difference.

The percentage of lead dioxide plus the percentage of combined lead monoxide gives the percentage of red lead present in the original sample. Having obtained the percentage of combined

Dingler's polytech. Journ. (1889), 271, 472.

lead monoxide, the amount of each of the oxides Pb_3O_4 and Pb_4O_5 which compose the total red lead present in the sample is ascertained by reference to Table II.

d. Total lead.—This determination serves simply as a check on the other determinations.

Treat a 0.2-gram sample with 30 cubic centimeters of 10 per cent nitric acid, boil until all red lead is completely changed to the black dioxide, cool, and add 20 cubic centimeters of sulphuric acid (1 part H_2SO_4 to 5 parts H_2O). Boil a few minutes. The soluble lead nitrate is changed to lead sulphate. Now add 2 cubic centimeters of concentrated hydrochloric acid, and the lead peroxide is changed to lead chloride.

Evaporate to white fumes, cool, add 10 cubic centimeters of water, and again evaporate to fumes. The lead chloride is converted to lead sulphate. The lead is now determined as sulphate as in the determination of free plus combined lead monoxide. In the presence of insoluble matter more accurate results are, of course, obtained by dissolving the lead sulphate in ammonium acetate and reprecipitating.

As red lead is only very slightly hygroscopic, moisture determinations are seldom necessary. Occasionally, adulterated, artificially colored samples are encountered. In such cases, the adulteration is best detected by leaching with suitable solvents.[10]

In the case of rapid work, when only approximately accurate results are desired, it is not necessary to make a complete analysis. In the absence of insoluble matter, the free lead monoxide may be determined by leaching with lead nitrate solution. One hundred per cent—per cent free PbO=per cent red lead. In the presence of insoluble matter

> 100 per cent—(per cent free PbO+per cent insoluble matter)
> =per cent red lead.

This method of analysis gives very satisfactory results when applied to high-grade samples which contain only red lead, free litharge, and no insoluble matter.

As previously pointed out, the analysis of red lead sample A gave unsatisfactory results when the percentage of red lead was calculated from the PbO_2 content. My method of analysis and

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[10] Technical methods of testing miscellaneous supplies. *Bull. U. S. Dept. Agr., Bur. Chem.* (1908), **No. 109,** 20.

calculation when applied to the same sample gave the following results:

<div align="center">*Sample A.*</div>

	Per cent.
Insoluble matter	none
Lead dioxide (PbO$_2$)	27.02
Combined lead monoxide (PbO)	54.52
Free lead monoxide (PbO)	18.54
	100.08
Lead dioxide (PbO$_2$)	27.02
Combined lead monoxide (PbO)	54.52
Red lead	81.54

1 gram of original sample contains $\begin{cases} 0.8154 \text{ gram of red lead.} \\ 0.5452 \text{ gram PbO combined.} \end{cases}$
Combined PbO in red lead proper = 66.86 per cent.

From Table II, 66.86 per cent combined PbO corresponds to a mixture of (80 per cent Pb$_3$O$_4$+20 per cent Pb$_4$O$_5$).

$$81.54 \times 0.80 = 65.23 \text{ per cent Pb}_3\text{O}_4 \text{ in original sample.}$$
$$81.54 \times 0.20 = 16.31 \text{ per cent Pb}_4\text{O}_5 \text{ in original sample.}$$

According to this method of calculating results, the analysis of sample A would be:

		Per cent.
Insoluble matter		none
PbO (litharge)		18.54
Red lead $\begin{cases} \text{Pb}_3\text{O}_4 \text{ (minium)} \\ \text{Pb}_4\text{O}_5 \end{cases}$		65.23
		16.31
		100.08

When the lead content is computed from these data and checked by a total lead determination, the following results are obtained:

	Per cent.
Total Pb by direct determination	91.37
Total Pb by direct calculation	91.21
Difference	0.16

By this method of calculation the total lead determination serves as a check on the entire analysis and the agreement between the calculated and determined total lead content of the sample is very close.

In Table III are given the data for a number of samples of red lead which have been investigated in accordance with this method of analysis and calculation.

TABLE III.—*Analyses and composition of red lead.*

Sample.	A.	B.	C.	D.	E.	F.	G.	H.
Insoluble matter	none	0.51	none	none	none	0.08	none	none
Free PbO	18.54	23.76	27.74	6.56	29.22	41.86	21.54	5.36
Red lead:								
PbO$_2$	27.02	24.53	24.76	31.28	23.18	19.80	26.30	31.96
Combined PbO	54.52	50.92	47.82	62.02	46.74	38.46	52.18	62.52
Red lead as obtained from Table I:								
Pb$_3$O$_4$	65.23	55.08	66.05	78.37	55.94	51.85	65.92	83.14
Pb$_4$O$_5$	16.31	20.37	6.53	14.93	13.98	6.41	12.56	11.84
Total Pb determined	91.37	89.90	91.20	90.65	90.86	91.11	91.13	90.83
Total Pb calculated	91.21	90.55	91.58	90.74	90.58	91.23	91.20	90.68
Total (insoluble matter + free PbO + Pb$_3$O$_4$ + Pb$_4$O$_5$)	100.08	99.72	100.32	99.96	99.14	99.70	100.02	99.84

As shown by the figures, there is a close agreement between the calculated total lead content and that obtained by direct determination.

As shown by the data presented in Table III, the method of analysis and calculation gives very accurate results.

Although many investigations on red lead have been carried out, its exact composition is still in doubt. The formula is usually written Pb$_3$O$_4$. Several investigators regarded it as a mixture of Pb$_3$O$_4$ and Pb$_4$O$_5$. Lowe considered it a mixture of Pb$_4$O$_5$ and PbO. Milbauer [11] calculated his results on the supposition that it is only Pb$_3$O$_4$.

According to the results, it would appear that red lead as ordinarily prepared consists of a mixture of the oxides Pb$_3$O$_4$, Pb$_4$O$_5$, and PbO, and the exact composition of any particular sample depends upon the conditions of manufacture which establish the equilibrium of the various component oxides.

[11] *Chem. Zeitg.* (1909), **33**, 513.

EDITORIAL

COPRA SPOILAGE ON A LARGE SCALE

One plate

The Swedish freight steamship *Nippon,* with a large cargo composed chiefly of dried coconut meat, or copra, was driven upon Scarborough Reef during a severe typhoon in May, 1913. The reef lies off the west coast of Luzon, and is practically submerged even during periods of low tide. The unfortunate vessel was firmly held by the coral, and the copra in the various holds was thus alternately submerged and exposed to a greater or less extent by the fluctuations of the tides.

The conditions thus presented unique opportunities to study the spoilage of copra on a very large scale. The salvage crew boarded the *Nippon* several days after the disaster, and found the hatches tightly closed. It was necessary to lighten the vessel before attempting to drag it into deep water. During an attempt to investigate the holds preparatory to discharging the copra, one member of the crew was fatally overcome by noxious gases and several others were rescued with difficulty. This dangerous condition persisted even after the holds had been open several days, and greatly interfered with the work of salvage. Every one who stayed below for a short time was affected with giddiness and marked palpitation of the heart, followed by unconsciousness unless immediate relief was sought in the open air. The eyes became seriously inflamed, and contact with water in the holds resulted in burns and sores.

The condition appeared so remarkable that an investigation by the Bureau of Science to explain the causes of the trouble was decided upon, and I was detailed to undertake the work. It was desirable to ascertain the nature of the poisonous gas and the caustic products present in the bilge water, not only in their bearing on the health of the workmen employed on the *Nippon,* but also as throwing light on the very important problem of copra deterioration.

Pumps had been installed on the *Nippon* before this investigation was started, and were regularly operated during the day. The sea water that penetrated during the night through the

various leaks was thus partially removed. In spite of the daily circulation established, it was possible to obtain samples of bilge water containing sufficient decomposition products for partial identification. It was found that bacterial action was taking place throughout the mass of copra, with the production of a large amount of hydrogen sulphide. Distinct tests for this gas were obtained in the open air at a distance of about 150 meters from the scene of the wreck, and vessels stationed near to render assistance were completely blackened within a short time. The hydrogen-sulphide-producing organism was found to be a motile rod. It appeared to act on the cellular tissue and cause an extraordinary selective destruction of the copra. One of the crew volunteered to obtain a sample of bilge water early in the morning before pumping was started. Accordingly, I left a bottle with him the preceding evening, with directions to fill it and immediately wire on the rubber stopper. This sample was carried to Manila for experimental purposes, and opened some days later in the laboratory. It consisted entirely of coconut oil, of slightly dark color and disagreeable odor. No water was gathered with the oil, indicating that the amount of free oil in the hold at that time must have been considerable, but owing to the darkness its presence had not been noted. Unfortunately, the sample bottle was made of opaque blue glass, with the result that I had no intimation of its true contents until after my return to Manila. Moreover, the floating débris of discharged copra had already rendered the adjacent surface of the ocean oily and effectively masked the effect of free oil which must have been pumped out early in the morning. The bacterial action had broken down the cellular tissue of the copra and liberated the oil. This oil contained 60 per cent free oleic acid.

The water passing through the copra was decidedly acid, a specimen taken late in the afternoon containing 0.5 per cent calculated as sulphuric acid. The acidity must have been much greater before the pumps were installed, and accounted for the caustic action of the water. Sulphurous and sulphuric acids were identified in the water, accompanied by various organic acids with indol and skatol resulting from decomposition. The action of this poisonous water was very severe, causing intense smarting where it came in contact with the skin, accompanied by very pronounced swelling of the testicles. These evil effects were mitigated by frequent bathing in salt water, and a shower was maintained on the deck for this purpose. This acid water was being pumped continually into the open sea, and the decaying copra was dis-

charged as rapidly as possible. The relatively large amount of free acidity thus produced may be judged from its effect on a bronze propeller shaft used on one of the ship's small launches. The portion exposed to the water was reduced to about one-half its original diameter (Plate I). It should be remembered that this was corroded, not in a protected bay or harbor, but in the open sea.

It is very probable that the many instances of deterioration known to take place during the shipment of copra are repetitions of the above conditions on a small scale. Sea captains have frequently informed me that it was always considered unwise to remain long in holds filled with copra. This finds its explanation in the slow production of toxic hydrogen sulphide. The rate of bacterial action depends upon the care used in preparing the copra and the degree of moisture present. With carefully dried copra, the deterioration due to hydrogen-sulphide-producing and other organism will be at a minimum, although it is doubtful if it can be entirely avoided until more satisfactory and sterilizing methods of preparation are generally employed.

DAVID S. PRATT.

128668——5

ILLUSTRATION

FIG. 1. Bronze propeller shaft, showing corrosive action of acid from decaying copra.

2. Side view of cross section of the shaft shown in fig. 1. (The ends were protected by the bearing and propeller, respectively.)

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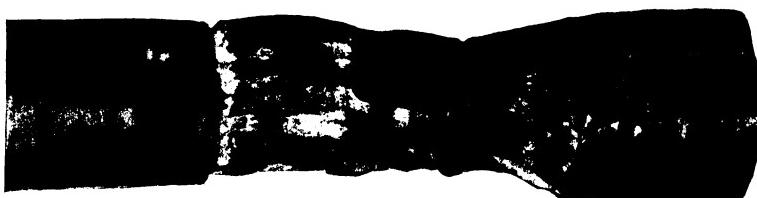
Fig. 1. Bronze propeller shaft, showing corrosive action of acid from decaying copra.

Fig. 2. Side view of cross section of the shaft shown in fig. 1.
(The ends were protected by the bearing and propeller, respectively.)

PLATE I.

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